

L Number	Hits	Search Text	DB	Time stamp
1	263	grafted adj (cellulose or cotton)	USPAT; US-PGPUB; EPO; JPO; DERWENT	2002/09/29 10:00
2	11	grafted adj (cellulose or cotton) adj fiber	USPAT; US-PGPUB; EPO; JPO; DERWENT	2002/09/29 10:01
3	11	grafted adj ((cellulose or cotton) adj fiber)	USPAT; US-PGPUB; EPO; JPO; DERWENT	2002/09/29 10:02
4	30233	AMPS or (acrylamide or acrylamido) adj5 (sulfonic adj acid)	USPAT; US-PGPUB; EPO; JPO; DERWENT	2002/09/29 10:04
5	24087	"HEMA" or hydroxyethyl adj (acrylate or methacrylate)	USPAT; US-PGPUB; EPO; JPO; DERWENT	2002/09/29 10:04
6	126938	isopropyl same alcohol or isopropanol	USPAT; US-PGPUB; EPO; JPO; DERWENT	2002/09/29 10:05
7	57656	polyacrylamide	USPAT; US-PGPUB; EPO; JPO; DERWENT	2002/09/29 10:05
8	17939	silver same nitrate	USPAT; US-PGPUB; EPO; JPO; DERWENT	2002/09/29 10:06
9	11	(grafted adj (cellulose or cotton)) and (grafted adj ((cellulose or cotton) adj fiber))	USPAT; US-PGPUB; EPO; JPO; DERWENT	2002/09/29 10:06
12	37	(grafted adj (cellulose or cotton)) and (isopropyl same alcohol or isopropanol)	USPAT; US-PGPUB; EPO; JPO; DERWENT	2002/09/29 10:07
13	3	(AMPS or (acrylamide or acrylamido) adj5 (sulfonic adj acid)) and ((grafted adj (cellulose or cotton)) and (isopropyl same alcohol or isopropanol))	USPAT; US-PGPUB; EPO; JPO; DERWENT	2002/09/29 10:07
14	34429	vinyl adj monomer	USPAT; US-PGPUB; EPO; JPO; DERWENT	2002/09/29 10:08
15	33	(grafted adj (cellulose or cotton)) and (vinyl adj monomer)	USPAT; US-PGPUB; EPO; JPO; DERWENT	2002/09/29 10:08
17	5	(isopropyl same alcohol or isopropanol) and (polyacrylamide and ((grafted adj (cellulose or cotton)) and (vinyl adj monomer)))	USPAT; US-PGPUB; EPO; JPO; DERWENT	2002/09/29 10:13
18	45	polyacrylamide and ((grafted adj (cellulose or cotton)) or (grafted adj (cellulose or cotton) adj fiber))	USPAT; US-PGPUB; EPO; JPO; DERWENT	2002/09/29 10:13

19	5	("HEMA" or hydroxyethyl adj (acrylate or methacrylate)) and (polyacrylamide and ((grafted adj (cellulose or cotton)) or (grafted adj (cellulose or cotton) adj fiber)))	USPAT; US-PGPUB; EPO; JPO; DERWENT	2002/09/29 10:17
22	3	(isopropyl same alcohol or isopropanol) and ((AMPS or (acrylamide or acrylamido) adj5 (sulfonic adj acid)) and ((grafted adj (cellulose or cotton)) or (grafted adj (cellulose or cotton) adj fiber)))	USPAT; US-PGPUB; EPO; JPO; DERWENT	2002/09/29 10:19
23	548185	alcohol	USPAT; US-PGPUB; EPO; JPO; DERWENT	2002/09/29 10:19
24	6	((AMPS or (acrylamide or acrylamido) adj5 (sulfonic adj acid)) and ((grafted adj (cellulose or cotton)) or (grafted adj (cellulose or cotton) adj fiber))) and alcohol	USPAT; US-PGPUB; EPO; JPO; DERWENT	2002/09/29 10:20
21	9	(AMPS or (acrylamide or acrylamido) adj5 (sulfonic adj acid)) and ((grafted adj (cellulose or cotton)) or (grafted adj (cellulose or cotton) adj fiber))	USPAT; US-PGPUB; EPO; JPO; DERWENT	2002/09/29 10:22
20	2	(isopropyl same alcohol or isopropanol) and (("HEMA" or hydroxyethyl adj (acrylate or methacrylate)) and (polyacrylamide and ((grafted adj (cellulose or cotton)) or (grafted adj (cellulose or cotton) adj fiber))))	USPAT; US-PGPUB; EPO; JPO; DERWENT	2002/09/29 10:23
16	8	polyacrylamide and ((grafted adj (cellulose or cotton)) and (vinyl adj monomer))	USPAT; US-PGPUB; EPO; JPO; DERWENT	2002/09/29 10:24
11	6	(isopropyl same alcohol or isopropanol) and (((grafted adj (cellulose or cotton)) and (grafted adj ((cellulose or cotton) adj fiber))) or ((grafted adj (cellulose or cotton)) and (AMPS or (acrylamide or acrylamido) adj5 (sulfonic adj acid))))	USPAT; US-PGPUB; EPO; JPO; DERWENT	2002/09/29 10:26
10	9	(grafted adj (cellulose or cotton)) and (AMPS or (acrylamide or acrylamido) adj5 (sulfonic adj acid))	USPAT; US-PGPUB; EPO; JPO; DERWENT	2002/09/29 10:28

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20	2	(isopropyl same alcohol or isopropanol) and (("HEMA" or hydroxyethyl adj (acrylate or methacrylate)) and (polyacrylamide and ((grafted adj (cellulose or cotton)) or (grafted adj (cellulose or cotton) adj fiber))))	USPAT; US-PGPUB; EPO; JPO; DERWENT	2002/09/29 10:23
16	8	polyacrylamide and ((grafted adj (cellulose or cotton)) and (vinyl adj monomer))	USPAT; US-PGPUB; EPO; JPO; DERWENT	2002/09/29 10:24
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10	9	(grafted adj (cellulose or cotton)) and (AMPS or (acrylamide or acrylamido) adj5 (sulfonic adj acid))	USPAT; US-PGPUB; EPO; JPO; DERWENT	2002/09/29 10:29
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27	1	(grafted adj (cotton or cellulose)) and (AMPS or (acrylamide or acrylamido) same (sulfonic adj acid))	USOCR	2002/09/29 10:30
25	23	grafted adj (cotton or cellulose)	USOCR	2002/09/29 10:31
28	137066	alcohol	USOCR	2002/09/29 10:31
29	11	(grafted adj (cotton or cellulose)) and alcohol	USOCR	2002/09/29 10:31

Patent Examiner's Tools

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 ocr L28: (137066) alcohol
 ocr L29: (11) 25 and 28
 L30: (268) 4 same 7
 L31: (177) (6 or 23) and 30
 L33: (4) 8 and 32
 L32: (23) 5 and 31
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1	<input type="checkbox"/>	<input type="checkbox"/>	US 20020095080 A1	20020718	20	Electrode array and sensor attachment system for noninvasive nerve location and	600/393	
2	<input checked="" type="checkbox"/>	<input type="checkbox"/>	US 20010024713 A1	20010927	7	Ink jet recording material	428/195	
3	<input checked="" type="checkbox"/>	<input type="checkbox"/>	US 6364477 B1	20020402	7	Ink jet recording element containing polymeric particles	347/105	
4	<input type="checkbox"/>	<input checked="" type="checkbox"/>	US 6294158 B1	20010925	7	Cosmetic composition containing an anionic polymer and an acrylic terpolymer,	424/70.1	424/401; 424/70.16;
5	<input checked="" type="checkbox"/>	<input type="checkbox"/>	US 6228348 B1	20010508	8	Composition in the form of an oil-in-water emulsion comprising an acrylic terpolymer	424/59	424/401; 424/70.1
6	<input checked="" type="checkbox"/>	<input type="checkbox"/>	US 5981159 A	19991109	30	Photographic material	430/546	430/545; 430/552;
7	<input type="checkbox"/>	<input checked="" type="checkbox"/>	US 5688855 A	19971118	9	Thin film hydrophilic coatings	524/505	524/113; 524/323;
8	<input checked="" type="checkbox"/>	<input type="checkbox"/>	US 5627145 A	19970506	7	Composition and method for controlling phosphonates tending to precipitate metal	507/224	210/642; 210/701;
9	<input type="checkbox"/>	<input type="checkbox"/>	US 5597386 A	19970128	20	Hair coloring composition comprising anti-hair antibodies immobilized on	8/405	424/70.6; 530/387.1;
10	<input type="checkbox"/>	<input type="checkbox"/>	US 5594047 A	19970114	38	Method for forming photographic dispersions comprising loaded latex	523/315	430/510; 430/517;
11	<input checked="" type="checkbox"/>	<input type="checkbox"/>	US 5582960 A	19961210	40	Photographic print material	430/508	430/546; 430/556;

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3,101,276

PROCESS FOR GRAFTING POLYMERS TO CELLULOSE SUBSTRATES

Robert William Hendricks, Claymont, Del., assignor to E. I. du Pont de Nemours and Company, Wilmington, Del., a corporation of Delaware.

No Drawing. Filed July 8, 1957, Ser. No. 670,369
9 Claims. (Cl. 117-56)

This invention relates to irradiation grafting of polymers to substrates and more particularly to an improvement in the polymer-grafting of cellulose substrates by the ionizing irradiation technique.

Recently it has been shown that polymers of ethylenically unsaturated polymerizable monomers may be formed in situ and affixed, i.e., grafted, to cellulose base materials by the action of ionizing radiation, applied either after or, in some instances, before the ethylenically unsaturated polymerizable monomer is placed in contact with the cellulose substrate. However, the efficiency of utilization of the ionizing radiation is extremely low, because the amount of available ethylenically unsaturated polymerizable monomer actually polymerized and grafted (i.e., chemically bonded) to the cellulose substrates is very slight. Thus, radiation-induced grafting of monomeric polymerizable compounds to cellulose as a means of obtaining desired property modification has been difficult to achieve, even by using such high radiation doses that heavy degradation resulted in the cellulose substrates.

An object of this invention, therefore, is to provide for the more efficient utilization of ionizing radiation in the grafting of polymers to cellulose substrates. Another object is to provide an improved process for forming and grafting to a cellulose substrate a polymer resulting from the polymerization of an ethylenically unsaturated monomer with the aid of ionizing radiation. A more specific object is to provide for the efficient utilization of ionizing radiation in grafting to regenerated cellulose film with polymers formed in situ from ethylenically unsaturated monomers. The foregoing and related objects will more clearly appear hereinafter.

The term "cellulose substrate" as used in this specification is intended to cover structures of native cellulose such as wood, wood pulp, paper, cotton structures, etc., as well as structures such as films, filaments, tubing, etc., of regenerated cellulose obtained, for example, by the well known viscose or cupra-ammonium process.

By the term "grafting," as used in this specification, it is meant that polymer formed is chemically bonded to the cellulose, and that the polymer is in the interstices as well as on the surface of the cellulose, depending upon the degree of penetration of monomer into the cellulose substrate.

The objects hereinabove stated are realized by the present invention which, briefly stated, comprises, in the process of forming and grafting polymers to cellulose substrates wherein a cellulose substrate is subjected to ionizing radiation and an ethylenically unsaturated monomer is brought into contact with said substrate and is polymerized in situ as a result of the action of said ionizing radiation, the improvement which comprises swelling the substrate by incorporating therein at least 15% by weight, based on the weight of substrate, of a water-soluble, non-polymerizable swelling agent for cellulose, and thereafter subjecting said substrate to said ionizing radiation.

The term "water-soluble" swelling agent as employed herein is intended to cover water itself, as well as non-polymerizable water-soluble acids, bases, and salts which serve to swell cellulose, and which are soluble in effective proportions, and swelling agents which are miscible with water.

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Swelling is a characteristic which is closely associated with most cellulose reactions. A solid is said to swell when it imbibes liquid while at the same time, its dimensions are enlarged, its cohesion is diminished, and it does not lose its apparent homogeneity. Cellulose fulfills all of the conditions for complex swelling and associated phenomena. The type and extent of swelling for any given condition depends upon the nature of the swelling agent, its specific interaction with cellulose, and the nature of the order-disorder structure of the cellulose sample. An example of cellulose swelling is the swelling of cellulose in water. As soon as water absorption begins, the cellulose starts to swell; the swelling increases in regular fashion as the total absorbed water increases and obtains its maximum value upon immersion of cellulose in excess water. Swelling beyond the water-swollen dimension takes place when the celluloses are immersed in certain aqueous solutions of acids, bases, or salts. The order of swelling power of the salts follow the well known lyotropic series, the more hydrated ions being the most effective swelling reagents. The decreasing order of swelling for the various cations and anions are as follows:¹



Swelling beyond the water-swollen conditions is also caused by aqueous solutions of various organic compounds such as thiourea, chloralhydrate, resorcinol, and benzenesulfonates.

In the process of this invention, the swelling agent is preferably a liquid, although it may be vapor, and is incorporated into the cellulosic shaped article prior to irradiation. The means used to accomplish this incorporation are not critical as long as the swelling agent is uniformly incorporated into the cellulosic material. In most cases, it is simplest to soak the cellulosic material in the swelling agent until the desired amount of swelling agent has been incorporated into the cellulosic material. This method is particularly useful with cellulosic substrates, such as films and filaments. (Details of Swelling Mechanisms of Cellulose, see High Polymers, vol. V, 2d ed., Cellulose, Ott; Spurlin, part I, pages 317-338.)

It is essential that at least 15% by weight of swelling agent be incorporated in the cellulose substrate in order to insure a positive swelling action over and above that incident to the normal moisture content of the substrate due to atmospheric conditions.

The preferred swelling agents in this invention are those materials which are liquid at temperatures in the range of 0°-50° C., i.e., the range in which the effect of radiation is at the maximum. Typical examples of such agents are aqueous systems, such as 10% caustic, 10% acid, water alone, water-glycerol, aqueous salt solutions, as well as organic systems, such as ethanol, ZnCl₂-methanol, glycerol, glycerol-toluene, glycerol-urea, ammonium sulfamate and/or combinations thereof.

The term "ionizing radiation" is meant to include both radiation in the form sometimes regarded as particle radiation and radiation in the form sometimes regarded as ionizing electromagnetic radiation.

By "particle radiation" is meant an emission of accelerated electrons or nuclear particles such as protons, neutrons, alpha particles, deuterons, beta particles, or the like, so that said particles impinge upon the cellulosic material undergoing irradiation. The charged particles may be accelerated by means of a suitable voltage gradient, using such devices as a cathode ray tube, a resonant cavity accelerator, a Van de Graaff accelerator,

¹ High Polymers, vol. V, 2nd Ed., Cellulose, Ott; Spurlin, part I, page 319.

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a betatron, a synchrotron, cyclotron, or the like, as is well known to those skilled in the art. Neutron radiation may be produced by bombardment of selected light metal (e.g., beryllium) targets with high energy positive particles. In addition, particle radiation suitable for carrying out the process of the invention can be obtained from an atomic pile, or from radioactive isotopes or from some other natural or artificial radioactive materials.

By "ionizing electromagnetic radiation" is meant radiation of the type produced when a metal target (e.g., tungsten) is bombarded by electrons possessing appropriate energy. Such radiation, conventionally termed X-ray, will have a short-wave length and a spectral distribution of energy at longer wave lengths determined by the target material and applied voltage. In addition to X-rays produced as indicated above, ionizing electromagnetic radiation suitable for carrying out the process in the invention can be obtained from a nuclear reaction ("pile") or from natural or artificial radioactive material (e.g., cobalt-60). In all of these latter cases, the radiation is conventionally termed gamma rays. While gamma radiation is distinguished from X-radiation only with reference to its origin, it may be noted that the spectral distribution of X-rays is different from that of gamma rays, the latter frequently being essentially monochromatic, which is not the case with X-rays produced by electron bombardment of a target.

It is recognized that the energy characteristics of one form of ionizing radiation can be expressed in terms which are appropriate for another form. Thus, it is acceptable to refer to energy equivalents between, for example, radiation commonly considered particle radiation and radiation commonly considered as wave or electromagnetic radiation. In the latter case, reference can be made to the energy of the individual photons. In the process of this invention, radiation which has an energy equivalent of an electron beam of at least 0.1 mev. (million electron volts) may be employed. Radiation with energy equivalent to an electron beam of 0.75 mev. to 2 mev. to 5 mev. is preferred where radiation of this energy is available at low cost and provides adequate penetration for the process. Radiation with an energy equivalent to an electron beam of 0.75 mev. and over (i.e., 0.75 mev. up to 2 and 5 mev.) is preferred where high penetration is desired. This may be particularly desirable in continuous operation. Thus, the choice of radiation energy level in excess of 0.75 mev. will depend upon the cost and penetration desired.

A minimum exposure of ionizing radiation of at least 0.001 watt-sec./cm.² of the swollen cellulosic material is necessary since lower degrees of exposure do not give adequate activation for initiating polymerization and grafting. The amount of polymerization and grafting in the contacting step usually increases with increasing degrees of exposure. Upper exposure limits depend on the amount of polymerization and grafting desired and on the radiation reactivity of the polymerizable monomer, as well as the stability of the base film. Exposures as high as 500-1000 watt-sec./cm.² may be employed; however, exposures greater than 125 watt-sec./cm.² usually result in heavy degradation of the cellulosic material. The exposure may be carried out at one slow pass or in several faster ones and may be conducted at any convenient amperage.

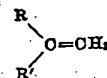
The temperature at which the irradiation step is carried out may be varied widely; irradiation temperatures, preferably, are within the range between the melting and boiling point of the swelling agent; but more specifically, in the range of 0°-50° C., since the maximum effect of the radiation is obtained in this temperature range. However, the temperature should not exceed the degradation temperature of the swollen cellulosic material and of polymerizable monomer present.

As examples of principal types of ethylenically un-

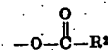
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saturated monomeric compounds useful in the present invention, there may be mentioned the monomeric unsaturated polymerizable compounds in which the unsaturation is due to terminal ethylenic groups, acrylic and methacrylic acids, esters, nitriles, and amides—for example, acrylonitrile, glycidyl methacrylate, methylmethacrylate; vinyl and vinylidene halides, e.g., vinyl chloride, vinyl fluoride, vinylidene chloride, vinylidene fluoride, vinyl carboxylates, e.g., vinyl acetate, vinyl trimethylacetate; vinyl aryls, e.g., styrene and vinyl naphthalene; and other vinyl derivatives such as methyl vinyl ketone, vinyl isobutyl ether and vinyl ethyl ether. Olefins, such as ethylene and isobutylene as well as mixtures of ethylenically unsaturated monomeric compounds such as ethylene/vinyl chloride, acrylonitrile/isobutylene, ethylene/vinyl acetate, isobutylene/vinyl acetate, vinyl acetate/allylidene diacetate, vinyl acetate/vinyl methyl ether may also be grafted to cellulose substrates by the present process of this invention.

The preferred ethylenically unsaturated monomers are those of the formula:



where R is selected from the group consisting of (a) the halogens, (b)



where R² may be H, or an alkyl or aryl group, (c) —CN, (d)



where R³ is an alkyl or aryl group, and (e) —OR⁴, where R⁴ is an alkyl or aryl group, and R' is selected from the group consisting of H, the halogens, alkyl and aryl groups.

The polymerizable ethylenically unsaturated monomer may be in contact with the swollen cellulosic substrate during irradiation, but its presence at that time is not essential. The radiation activates the swollen cellulosic substrate toward polymerization and grafting of the monomer, and, if the polymerizable monomer is applied within the period during which the swollen cellulosic substrate remains active, grafting of the polymerizable monomer takes place. The time which may elapse between irradiation and the contacting step will vary with radiation exposure, temperature, atmosphere of the storage, and the chemical nature of the polymerizable monomer. A storage time of not over 5 minutes between steps is usually preferred, and substantially immediate contact (less than one second) is frequently desirable. It has been observed, however, that the effects of the irradiation can be sustained for longer periods of time i.e., weeks and even months, if the irradiated swollen cellulosic substrate is kept in an inert atmosphere such as under nitrogen, argon, helium, or the like and/or stored at low temperatures such as at -80° C. In general, the lower the temperature at which the irradiated swollen cellulosic substrate is stored, the longer time the swollen cellulosic substrate remains active toward polymerization and grafting of the polymerizable monomer. It is thus possible to irradiate the swollen cellulosic substrate at a site of available irradiation and then, by maintaining suitable storage conditions, to ship the irradiated swollen cellulosic substrate to another site for carrying out the contacting step. However, the grafting yield at a given radiation exposure is greater when the polymerizable monomer is in contact during radiation and, for economic reasons, this represents the preferred practice of this invention.

It may be desirable to incorporate an organic softener into the aqueous swelling agent (e.g., glycerol/water solutions are used as softeners for regenerated cellulose film and therefore a solution of this type could also be em-

employed as a swelling agent wherein the water is more readily removed in the final step than the glycerol, thus avoiding the need of having to add glycerol in an additional operation in the manufacture of regenerated cellulose film). Softeners such as disclosed in King U.S. Patent No. 2,074,336, Underwood U.S. Patent No. 2,074,349, Snyder U.S. Patent No. 2,087,008, and Rothrock U.S. Patent No. 2,328,679 may, if desired, be incorporated prior to irradiation and grafting without adversely affecting the process of the present invention.

Cellulosic materials pretreated with anchoring agent resins, such as a urea-aldehyde resin, phenol-formaldehyde resin, ketone-aldehyde resin, amine modified urea-aldehyde resin, alcohol modified urea-aldehyde resin, etc., disclosed, for example, in Charch and Bateman U.S. Patent No. 2,159,007, Pitzl U.S. Patent No. 2,432,542, Chapman U.S. Patent No. 2,533,557, and Wooding U.S. Patent No. 2,546,575, as well as organic titanium compounds, disclosed, for example, in U.S. patent applications of Brill, S.N. 378,175, filed September 2, 1953, now abandoned, Brill S.N. 489,800, filed February 21, 1955, now U.S. Patent No. 2,943,955, and Haslam U.S. Patent No. 2,768,909, may be employed without detrimentally affecting the process of the invention.

It has been found that the grafting are primarily attached to the substrate and that the swelling agent may be subsequently removed with essentially no loss of the graftings. This makes it possible to greatly increase the efficiency of radiation by employing large amounts of swelling agents (which might undesirably affect the grafted substrate if left in place) and, removing part or all of the swelling agent by any convenient expedient. Any unreacted or ungrafted material may be extracted by employing a solvent for the swelling agent which is also a solvent for the unreacted or ungrafted material. This procedure is convenient, but is not essential to the process. Mechanical removal—such as by heat and/or vacuum are of particular advantage in the case of aqueous systems.

The specific form or shape of the swollen cellulose substrate employed is not a factor in the invention. It may be a film as illustrated in the following examples, or it may be a molded object, fiber, knitted or woven fabric, tube, extruding molding, or the like. Of particular advantage, however, are native cellulose, wood pulp, lumber, vulcanized fiber board, film, fiber, fabric, and various extruded forms, since they are readily adaptable to continuous operation according to the process of this invention.

In the continuous manufacture of regenerated cellulose film, such as disclosed in Brandenberger U.S. Patent No. 1,548,864, the process of the invention may be employed as an integral part of the continuous manufacture. For example, the gel regenerated cellulose film (swollen 200–350% with water and/or water-softener) may be then passed into a liquid monomer bath and then substantially immediately thereafter irradiated prior to the modified gel regenerated cellulose film passing through the conventional dryer, thus reducing the modified film to the desired moisture and softener content.

The following specific examples will further serve to illustrate the principles and practice of this invention. Percentage compositions are by weight unless otherwise indicated:

EXAMPLE 1

A weighed strip (87.3 mg.) of regenerated cellulose film (conditioned to room temperature and humidity, unsoftened and unsized), 0.0013" thick was soaked for approximately 10 minutes in an aqueous 10% NaOH solution, then thoroughly rinsed in tap water, reweighed (246 mg.) and placed in a cell consisting of thin glass plates spaced with strips of 7/4 mil "Mylar" (Du Pont polyester film). The preswelling represented a 182% weight gain over the original dry weight. A second weighed strip of

identical regenerated cellulose film not soaked or otherwise conditioned was placed in another cell; then both cells were filled with vinyl acetate and sealed. The cells were given 5 standard passes in the Van de Graaff accelerator (a "standard" pass consisting of a sample passing under an electron beam at a speed of 2 cm./sec., using a scan width of 20 cm., sample-to-window distance of 10 cm., beam current of 250 microamperes, an electron energy of 2 mev.). Under the conditions used, one standard pass is equivalent to approximately 1.5 megarads in the irradiated film and total exposure was 62.5 watt-sec./cm.². No external cooling was used during irradiation. The samples were removed from the cells and soaked overnight in methylethyl ketone, a solvent for polyvinyl acetate to remove the ungrafted homopolymer. After a final acetone rinse, the films were dried in a vacuum drying oven at 90° C. for 1.5 hours at 0.1 mm., and then conditioned to room humidity and weighed; >98% of the swelling agent was removed. The originally swollen irradiated sample was found to have increased in weight (127.3 mg.) by 46%, based on the original dry weight, while the originally unsoaked irradiated sample lost 2.6% in weight.

Infra-red spectra analyses were run on both the samples—the originally swollen sample possessed a very strong band at 7.5 μ , characteristic of polyvinyl acetate, in the spectra, while the spectrum of the originally unswollen sample showed no band at this wave length.

EXAMPLE 2

Weighed strips of regenerated cellulose film were treated as in Example 1, except that vinylidene chloride, freed of inhibitor by washing with caustic, was used in the cells, which were given 5 standard passes while being cooled by a wet ice bath. The presoaked sample had a 180% weight gain. After mechanical removal of a deposit of homopolymer, overnight extraction with dioxane, oven drying, and conditioning at room temperature, the films were weighed; >98% of the swelling agent was removed. The originally swollen film had increased in weight by 5.5% while the unswollen film had lost 1.8% in weight.

EXAMPLE 3

Weighed strips of regenerated cellulose film were treated as in Examples 1 and 2, except that distilled acrylonitrile was used as the monomer. The cell containing the preswollen film, 182% weight gain, was given one standard pass without external cooling, after extraction in hot dimethyl formamide, drying, conditioning, and weighing, it was found that the originally preswollen sample had gained 14.7% in weight based on the original dry weight. The film had >98% of the swelling agent removed. The second, unswollen film, given 5 standard passes, was not extracted, but after drying and conditioning, and reweighing, had gained only 3.9% by weight. Infra-red spectra analyses were run on both the samples—these originally swollen showed a strong band at 4.45 μ , characteristic of polyacrylonitrile, while the unswollen sample contained no band at this wave length.

EXAMPLE 4

Two strips of regenerated cellulose film (A and B) were weighed. Film A was swollen in 10% aqueous HCl for approximately 10 minutes, then rinsed with water as in the preceding examples and had a 45% weight gain; film B was merely soaked in water for approximately 10 minutes and had a 104% weight gain. The films were irradiated in cells filled with vinyl acetate as in Example 1, using 5 standard passes without external cooling, and were then extracted, dried, conditioned, and weighed as in Example 1. Film A gained 59%, and film B had gained 51%. Films A and B had 100% of the swelling agent removed. Infra-red spectra analyses were run on both samples and in each case, the samples showed a very strong band at 5.7 μ , characteristic of polyvinyl acetate in the spectrum. The following series of examples and controls, tabu-

lated in Table I, illustrate the process of the invention. The examples were conducted in accordance with the procedure indicated in the preceding examples.

advantage, since the polyacrylonitrile modified vulcanized fiber board has greatly increased electrical resistance suitable for use with printed circuits.

Table I

Ex.	Cellulosic substrate	Monomer	Swelling agent	Percent swollen weight gain	Temp., ° C.	Passes/micro-amps.	Percent swelling agent removed	Percent weight gain
5	Regenerated cellulose film ¹	None	10% HCl in water	72	25	None	100	-14
	Do ¹	Vinyl acetate	None	72	25	5/250	100	-8
	Do	do	10% HCl in water	72	25	5/250	100	58
6	Cheese cloth ¹	Vinyl acetate	None	89	25	10/250	100	4
	Do	do	10% HCl in water	89	25	10/250	100	61
7	Cheese cloth ¹	Acrylonitrile	None	59	25	10/250	100	19
	Do	do	10% HCl in water	59	25	10/250	100	146
8	Brown Dur-Natus wood pulp ¹	Acrylonitrile	None	136	25	5/250	100	5
	Do	do	10% HCl in water	136	25	5/250	100	91
9	Gel regenerated cellulose film ¹	Divinyl benzene	None	180	25	2/25	100	0
	Do ¹	do	Water	180	23	0	100	7
	Do	do	do	164	23	2/25	100	17
10	Gel regenerated cellulose film ¹	50% glycidyl methacrylate in toluene	None	28	25	0	100	2.2
	Do ¹	do	do	25	25	1/250	100	2.9
	Do	do	Glycerol	>40	25	1/250	>99	5.8
11	Gel regenerated cellulose film ¹	Glycidyl methacrylate	None	25	25	0	100	2.5
	Do ¹	do	do	25	25	1/250	100	2.7
	Do	do	Glycerol	>40	25	1/250	>99	9.2
12	Regenerated cellulose film	Vinyl acetate	Water	104	-78	5/250	100	45
	Do	do	do	104	25	5/250	100	45
13	Regenerated cellulose film	Acrylonitrile	10% HCl in water	45	25	1/250	100	8
	Do	do	do	45	25	4/62.5	100	64
14	Regenerated cellulose film	Vinyl acetate	10% HCl in water	45	25	5/250	100	72
	Do	do	do	45	25	20/62.5	100	190

¹ Control.

In addition to the primary advantages of improved polymerization and increase in the grafting of the ethylenically unsaturated polymerizable monomer to the swollen cellulosic substrate, the present invention may be employed to secure a variety of other beneficial effects. For example, in fibrous and non-fibrous articles, such as paper, film and rigid and semi-rigid molded and extruded forms, it may modify such structures to improve the adhesion to various coating or laminating agents which it may be desirable to adhere thereto, to improve "slip," to produce flame retardant structures, to produce non-extractable fungicidal structures, to produce reinforced structures and to produce articles having increased resistance to heat and increased mechanical strength. It may be employed in textiles to effect ease of textile processability, overall appearance, adhesion, static propensity, hydrophilic or hydrophobic characteristics, abrasions, wear-resistance, laundering properties (dry cleaning), printability, and finishing treatments. Many other beneficial modifications may be produced, such as will occur to those skilled in the chemical arts.

More specifically, vinyl-phosphorous compounds are well known flameproofing additives for cellulosic materials and may be incorporated into cellulosic structures by the process of this invention—bis(chloroethyl) vinyl phosphonate is an example of this class. Vinyl-silane compounds are also well known waterproofing additives for the cellulosic materials which may be incorporated by the invention—vinyl dimethyl-chloro-silane and vinyl-ethoxy-dimethyl-silane are representative compounds. Graftings of less than 2% acrylonitrile to cellulosic materials are of particular advantage since it has been demonstrated that such acrylonitrile grafted cellulosic materials are highly resistant to mildew and fungi growths. And, in the manufacture of vulcanized fiber board, such as disclosed in Materials and Methods, September 1954, p. 110, by the $ZnCl_2$ process, the utilization of the process of the invention for incorporating therein polyacrylonitrile is of

I claim:

1. In the process of forming polymers on regenerated cellulose film wherein the surface of cellulose film is subjected to ionizing radiation and an ethylenically unsaturated monomer is applied to the surface of the film and is polymerized in situ as a result of the action of said ionizing radiation; the improvement which comprises swelling the regenerated cellulose film by incorporating therein at least 15% by weight, based on the weight of film, of a water-soluble non-polymerizable swelling agent for cellulose, and thereafter subjecting the surface of the resulting swollen film to said ionizing radiation.

2. The process of claim 1 wherein the dose of applied ionizing radiation is at least 0.001 watt-sec./cm.² of ionizing radiation of from 0.75 to 5 mev. energy.

3. The process of claim 1 wherein the swelling agent is an aqueous swelling agent for cellulose.

4. The process of claim 2 wherein the swelling agent is an aqueous sodium hydroxide solution.

5. The process of claim 2 wherein the swelling agent is an aqueous hydrogen chloride solution.

6. The process of claim 2 wherein the swelling agent is aqueous glycerol solution.

7. The process of claim 2 wherein said swollen structure is maintained at a temperature within the range of from 0°-50° C. during radiation.

8. The process which comprises incorporating in regenerated cellulose film at least 15% by weight of a water-soluble, non-polymerizable swelling agent for cellulose, applying to the resulting swollen substrate an ethylenically unsaturated monomer, and thereafter subjecting said swollen substrate to ionizing radiation of from 0.75 to 5 mev. energy for an exposure of at least 0.001 watt-sec./cm.².

9. In the process of forming polymers in regenerated cellulose shaped structures wherein the surface of a regenerated cellulose shaped structure is subjected to ionizing irradiation and an ethylenically unsaturated

monomer is applied to said surface and is polymerized in situ as a result of the action of said ionizing radiation, the improvement which comprises swelling the regenerated cellulose shaped structure by incorporating therein initially at least 15% by weight, based on the weight of said structure, of a water-soluble, non-polymerizable swelling agent for cellulose.

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PROCESS FOR RADIATION GRAFTING ONTO A PARTIALLY SWOLLEN CEL- LULOSIC SUBSTRATE

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No Drawing. Continuation of application Ser. No.
817,881, June 3, 1959. This application July 19,
1966, Ser. No. 571,375

Int. Cl. B01j 1/10, 1/12

U.S. Cl. 204—159.12

14 Claims

This application is a continuation of U.S. application
817,881 filed June 3, 1959 which is a continuation-in-part
of U.S. applications Nos. 500,032 filed Apr. 7, 1955 and
now abandoned and 503,792 filed Apr. 25, 1955 and now
abandoned.

This invention relates to a product and process. More
particularly it concerns a process for grafting an organic
compound to a fiber produced from a natural carbona-
ceous material of the class consisting of cellulose, protein
and isoprene polymer and the product formed thereby.

The fibers of nature, i.e. those from natural carbona-
ceous cellulose, protein and isoprene polymers have many
deficiencies when employed for apparel purposes. At-
tempts to cure these deficiencies by surface treatments
with resins, etc., have not been satisfactory. For example,
thin resin coatings on the filaments are not permanent to
laundering. Heavy deposits of resins, rendered more du-
rable and self-supporting by cross-linking, stiffen the fab-
ric, making it harsh and unpleasant to handle or wear.
Carried to an extreme, the fabric becomes bonded into a
stiff unitary structure lacking in aesthetic appeal and good
wear properties.

OBJECTS

It is an object of the present invention to provide a
process for grafting an organic compound to a textile
produced from a carbonaceous material of nature as de-
fined hereinafter.

Another object is to provide a textile formed from
a natural carbonaceous polymer which is permanently
modified to make it, for instance, more free from static,
more dyeable, more resilient or crease resistant or more
flame resistant, than textiles heretofore obtainable from
the said polymers. Products having moisture absorption,
hand and strength characteristics differing from the nat-
ural counterparts are also provided.

Still another object is to provide a process which com-
prises applying a highly fluid organic compound or highly
fluid solution of an organic compound to a textile formed
from natural or man-made polymer filaments and there-
after inducing chemical bonding between the said textile
and organic compound, producing a permanently modi-
fied filament and textile.

A further object is to provide a process for perman-
ently modifying a filament derived from a natural polymer
throughout its bulk comprising the sequence of applying
a suitable vinyl monomer to the surface of the filament,
permitting the monomer to penetrate through the filament,
exposing the structure to ionizing radiation to induce graft-
ing between the monomer and the filament and thereafter
scouring or extracting to remove any ungrafted modifier.

These and other objects will become apparent in the
course of the following specification and claims.

STATEMENT OF INVENTION

In accordance with the present invention, all of the
filamentary surfaces of a textile produced from a fiber-
forming carbonaceous material of nature of the class
consisting of cellulose, protein and isoprene polymer, are

coated with an organic compound modifier, a flowable ex-
cess being avoided when necessary to prevent inter-fila-
ment bonding at the radiation dose employed, subjecting
the combination to ionizing radiation, producing chemical
bonds between the textile and the organic compound and
finally extracting ungrafted excess of the said modifier.
For deep seated modifications the organic compound is
permitted to diffuse into the filamentary substrate prior to
the irradiation. Alternatively, the organic compound modi-
fier, especially when it is of high molecular weight, may
remain upon the surface of the textile during the irradi-
ation step, thus producing a uniform chemically grafted
coating on each filament. The organic compound modifiers
employed in the practice of this invention are either per se
highly fluid at the temperature at which they are applied
or they are employed in highly fluid solution so that they
readily migrate over the filament surfaces.

In a typical embodiment the process of the present in-
vention is applied to a yarn or tow, which after being
impregnated with organic compound modifier, is irradiated
and thereafter extracted to remove ungrafted material.
The product is then dried, and may be used as continuous
filament yarn, or alternatively, it may be cut to form
staple fiber which is then spun to yarn and woven to tex-
tiles following conventional procedure.

Alternatively, the textile may be wrung out or centri-
fuged prior to irradiation, to remove excess treating solu-
tion.

In a batch or a continuous process, it is merely neces-
sary to provide sufficient yarn "dwell time" in each step,
for instance by using multiple yarn passes during coating,
impregnation or irradiation, so that the desired result will
be obtained.

DEFINITIONS

By the term "textile produced from a fiber-forming
carbonaceous material of nature" is meant a structure pro-
duced from filaments or films having a cellulose, protein
or isoprene polymeric composition and formed in plant
or animal growth and to fiber- and film-forming deriva-
tives and regenerated forms of the natural carbonaceous
polymers such as protein, cellulose acetate and regenerated
cellulose.

By "graft copolymer" is meant a polymer which is
modified, after shaping, by chemically bonding thereto,
molecules of a chemically dissimilar organic compound.

By "irradiation" is meant the process by which energy
is propagated through space, the possibility of propaga-
tion being unconditioned by the presence of matter (as
distinguished from mere mechanical agitation in a ma-
terial medium such as is characteristic of energy produced
by a sonic or ultrasonic transducer), although the speed,
direction, and amount of energy transferred may be thus
affected.

By "ionizing radiation" is meant radiation with suf-
ficient energy to remove an electron from a gas atom,
forming an ion pair; this requires an energy of about
32 electron volts (ev.) for each ion pair formed. This
radiation has sufficient energy to non-selectively break
chemical bonds; thus, in round numbers radiation with
energy of about 50 electron volts (ev.) and above is ef-
fective for the process of this invention. The ionizing
radiation of the process of this invention is generally
classed in two types: high energy particle radiation, and
ionizing electromagnetic radiation. The effect produced by
these two types or radiation is similar, the essential requi-
site being that the incident particle or photons have suf-
ficient energy to break chemical bonds and generate free
radicals.

The preferred radiation for the practice of this invention
is high energy ionizing radiation, and has an energy
equivalent to at least 0.1 million electron volt (m.e.v.).

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Higher energies are even more effective; there is no known upper limit, except that imposed by available equipment.

By an "organic compound" is meant a material having the formula CX_n , where X is a member of the group consisting of hydrogen, halogen, nitrogen, nitrogen radical, oxygen, oxygen radical, sulfur, sulfur radical or organic radical. By "organic radical" is meant a radical predominantly hydrocarbon except for the presence of substituents immediately hereinbefore listed. Where one or more of the X's is organic radical, it is preferred that it be linked to the CX residue by a carbon-to-carbon bond. Furthermore, the C may be doubly bonded to no more than S= or O= atom; i.e., only one pair of X's may be replaced by a divalent oxygen or sulfur atom. Typical compounds included are hydrocarbons, alcohols, acids, ethers, ketones, esters, aldehydes, isocyanates, sulfonates, mercaptans, thioethers, disulfides, nitriles, nitro compounds, amines, amides and halides. Compounds with ethylenic unsaturation are especially preferred, since a minimum radiation dose is required to graft a given weight of modifier. However, non-polymerizable organic compounds (free from aliphatic unsaturation) are also readily grafted, to produce effective modification of polymer properties. Of these compounds, the chain transfer agents are preferred.

Another useful class of modifiers is the high molecular weight compounds, especially polymers. These compounds are readily and effectively grafted since a single site of attachment bonds a relatively large weight of modifier, due to the large molecular weight. The large molecule tends to prevent penetration by these modifiers, and hence they are especially useful in creating surface effects. The polymeric modifiers especially preferred for textile uses are those which may be applied to the textile as a low viscosity solution or melt, thus ensuring that each filament is completely coated.

EXPERIMENTAL PROCEDURES AND UNITS

Compositions are given in parts by weight or weight percent, unless otherwise noted.

Radiation dosages are given in units of "mrads" (millions of rads), a "rad" being the amount of high energy radiation of any type which results in an energy absorption of 100 ergs per gram of water or equivalent absorbing material. Alternatively, dosages may be indicated in terms of exposure in watt seconds per square centimeter of substrate treated.

The "standard washing" to which samples are subjected consists of a 30-minute immersion in 18 liters of 70° C. water contained in a 20-liter agitation washer. The wash solution contains 0.5% of detergent. The detergent employed is that sold under the trademark "Tide" of Procter and Gamble Company of Cincinnati, Ohio. This detergent contains, in addition to the active ingredient, well over 50% (sodium) phosphates (Chemical Industries, 60, 942, July, 1947). Analysis shows the composition to be substantially as follows:

	Percent
Sodium lauryl sulfate	16
Alkyl alcohol sulfate	6
Sodium polyphosphate	30
Sodium pyrophosphate	17
Sodium silicates and sodium sulfate	31

The static propensity of the fabric is indicated in terms of direct current resistance in ohms per square, measured parallel to the fabric surface, at 78° F. in a 50% relative humidity atmosphere. High values, reported as the logarithm (to the base 10) of the resistivity (log R) indicate a tendency to acquire and retain a static charge. A meter suitable for this determination is described by Hayek and Chromey, American Dyestuff Reporter, 40, 225 (1951).

Crease recovery is evaluated by crumpling a fabric in the hand, and observing the rate at which it recovers

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from this treatment. Numerical values are obtained using the Monsanto Crease Recovery Method, described as the "vertical strip crease recovery test" in the American Society for Testing Materials Manual, Test No. D1295-53T. In determining crease recovery by this method, the specimens are creased under a standard weight; the weight is then removed, and the recovery after 300 seconds is measured, averaging results obtained in the filling and warp directions.

The following examples are cited to illustrate the invention. They are not intended to limit it in any manner.

EXAMPLE 1

A sample of wool fabric is coated by being immersed in a solution of 16 parts polyethylene glycol 20,000¹ and 84 parts water, the solution having a viscosity of 119 centipoises at 25° C. The excess liquid is squeezed out. While still wet it is enclosed in an aluminum foil wrapper and subjected to electron irradiation in a 1 mev. resonant transformer with a beam-out current of 560 microamperes. The sample is placed on a conveyor belt which carries it through the electron beam at a rate of 16 inches per minute. At the sample location, the beam supplies irradiation of 5.6×10^6 rad (5.6 mrads) per pass. The sample is traversed back and forth across the beam until a total dose of 3 mrads is attained. The coated, irradiated fabric along with an uncoated, irradiated comparative control and a swatch of the original fabric are given 15 consecutive washings. After two washings the wool has a slightly waxy hand; after 15 washings, the hand is similar to the original, untreated fabric. The coated, irradiated sample retains its original dimension without unravelling at the edges. It has a log resistivity of 9.1. Both comparative controls unravel badly during washings. They are also observed to develop numerous small fibrous balls (known as "pills") on their surfaces, whereas the test fabric develops few, if any, pills. The log resistivity of each control sample is 13.3. Thus, by treatment according to the process of this invention, the wool has been made washable.

EXAMPLE 2

A piece of silk fabric is coated by being immersed in liquid methoxydecaethyleneoxy methacrylate. The excess reagent is squeezed out. While still wet it is wrapped in aluminum foil and irradiated, using a Van de Graaff generator under the conditions listed below:

Voltage mev.	2
Tube current, microamperes	290
Conveyor speed, in./min.	40
Dose per pass, mrads	2
Number of passes	20
Total dose, mrads	40

The coated, irradiated fabric is given 15 standard washings after which its log resistivity is 10.3. The filaments are not bonded together; no surface deposit is observed. The strength and hand of the original fabric are retained. A similarly irradiated control has a log resistivity of 13.3, while that of the original fabric is 12.9 after similar washings. Another control sample immersed in the methoxydecaethyleneoxy methacrylate, but not irradiated, and thereafter subjected to the 15 standard washings, shows no change in log resistivity over the original fabric.

EXAMPLE 3

A fabric woven from continuous filament cellulose acetate yarn is dipped in liquid methoxydecaethyleneoxy methacrylate and the excess liquid is squeezed out. The sample is then irradiated with the equipment and in accordance with the technique of Example 2 to a radiation dosage of 20 mrads. Washing removes surface deposits of ungrafted polymer. The log resistivity of the product

¹ The figure indicating molecular weight.

after 15 standard washings is 9.9. The value for the original fabric is 10.8.

EXAMPLE 4

A piece of cotton fabric is immersed in liquid methoxydecaethyleneoxy methacrylate and the excess liquid is squeezed out. The coated sample is then irradiated in the equipment and in accordance with the technique of Example 2 to a total radiation dosage of 20 mrad. After 15 standard washings the log resistivity of this sample is 9.6. This compares to a value for the original fabric after 15 standard washings of 10.8.

To illustrate the practice of this invention using X-rays, fabric samples in Examples 5 and 6 are immersed in the

After 15 standard washings, the treated irradiated sample is found to have shrunk about 20%, and to have acquired a delustered appearance. It has also become elastic, yet retained substantially all its original strength and has a bulkier hand as compared to a portion of the original material.

EXAMPLE 7

Rayon taffeta samples are soaked as shown in Table 1, then irradiated with 2 mev. electrons to give the indicated dose. After removing ungrafted material by the consecutive extractions listed, the weight gain is determined. In some cases, the sample is preswollen before irradiation.

TABLE 1

Sample No.	Swelling agent	Concentration of grafting agent	Dose, mrad	Extraction solvents	Weight gain, percent
7A.....	None.....	20% acrylonitrile in H ₂ O.....	2	Hot water, hot dimethyl formamide, hot water.	12.0
7B.....	do.....	50% diallylitaconate in CH ₃ OH.....	2	do.....	1.5
7C.....	CH ₃ OH.....	100% distilled styrene.....	2	Hot benzene, hot acetone, hot water.	11.7
7D.....	None.....	100% 1,2-disobutylene oxide.....	2	Hot CH ₃ OH, hot H ₂ O.....	0.4
7E.....	Water.....	50% methyl methacrylate in CH ₃ OH.....	2	CH ₃ OH, acetone, CH ₃ OH, H ₂ O.....	18.0
7F.....	None.....	50% methyl methacrylate in CH ₃ OH.....	2	do.....	1.1
7G.....	H ₂ O.....	100% vinyl acetate.....	2	Acetone.....	12.9
7H.....	None.....	50% 4-vinyl pyridine in H ₂ O.....	2	Hot water.....	8.5

chosen treating liquid, the excess liquid squeezed out, then each fabric sample while still wet, is wrapped in aluminum foil forming a first package. A set of untreated controls is also packaged. All the foil packages are combined into a pile 1/2 inch thick, and are then simultaneously irradiated as described hereinafter.

The samples are exposed to X-radiation using a resonant transformer X-ray machine marketed by the General Electric Company of Schenectady, N.Y., known as a "Two Million Volt Mobile X-Ray Unit." This machine is described by E. E. Charlton and W. F. Westendorf in the Proceedings of the First National Electronics Conference, p. 425, October 1944. The pile of packaged samples is placed in an open top box made from 1/8 inch sheet lead, and positioned so that the top sample is 8 cm. from the tungsten tube target. At this location, using a tube voltage of 2 mev., and a tube current of 1.5 milliamperes, the irradiation rate is 1.5 mrad per hour. The beam irradiates a circle about 3 inches in diameter; all fabric tests are made on the irradiated portion.

EXAMPLE 5

A sample of wool fabric is coated by being immersed in a solution of 16 parts polyethylene glycol 20,000 and 84 parts water. The excess liquid is squeezed out. While still wet it is enclosed in an aluminum foil wrapper and subjected to X-ray radiation as described above. The sample receives a total dose of 27 mrad. The coated, irradiated fabric along with an uncoated, irradiated comparative control and a swatch of the original fabric are given 15 consecutive standard washings. The coated, irradiated sample retains its original dimension and hand without unravelling at the edges. Both comparative controls unravel badly during washings. They are also observed to develop numerous small fibrous balls (known as "pills") on their surfaces, which were not observed on the treated irradiated test sample.

EXAMPLE 6

A fabric woven from continuous filament cellulose acetate yarn is immersed in a mixture of 30 parts maleic anhydride, 70 parts methoxydecaethyleneoxy methacrylate monomer and 100 parts of water and the excess liquid is squeezed out. The sample is then irradiated with the equipment and in accordance with the technique described for Example 5 to a radiation dose of 13.5 mrad.

Some of the more outstanding property changes of the grafted, modified fibers, compared to non-irradiated, non-grafted controls, are listed in Table 2.

TABLE 2

Sample No.	Property change
7A.....	Improved resilience, drier hand, water absorption reduced by 15 to 30%, improved crease retention on wetting, 20% increase in wet breaking strength.
7C.....	Water absorption decreased 10 to 15%.
7D.....	Fabric much less wickable than ungrafted control.
7E.....	Dry breaking strength increased 21%; wet, 26%.

EXAMPLE 8

A wool flannel sample is padded with a solution of 50% methyl acrylate in methanol, then irradiated with 2 mev. electrons to give a dose of 1 mrad. After removing ungrafted modifier, the weight gain is 8.1%.

The grafted sample is wetted with dilute aqueous ammonia, and a crease is pressed into it, using a steam iron. The fabric is washable, and the crease is retained even after a 50° C. detergent wash.

EXAMPLE 9

Samples indicated in Table 3 are soaked and irradiated as shown in Table 4.

TABLE 3

Sample No.	Substrate	Trade name
9A.....	Protein fiber from peanut protein.	"Ardil," ICI.
9B.....	Protein fiber from casein.....	"Fibrolane," Courtaulds.
9C.....	Protein fiber from seia.....	"Vicars", Virginia-Carolina Chem. Co.
9D.....	Cellulose triacetate fiber.	
9E.....	Saponified cellulose acetate fiber.	"Fortisan," Calanese.
9F.....	Natural rubber sheet.....	
9G.....	Wool.....	
9H.....	do.....	
9I.....	Silk.....	
9J.....	Cellulose acetate fiber.....	
9K.....	Cotton cleaning mop.....	
9L.....	Rayon taffeta.....	
9M.....	Rayon taffeta.....	
9N.....	Rayon taffeta, previously grafted with 12% polyacrylonitrile.	

1 Sample 9N is prepared by soaking a swatch of rayon fabric in methanol, then in 100% acrylonitrile followed by irradiation (2Mrep); ungrafted material is removed by hot extraction with water, dimethyl formamide, then water.

TABLE 4

Sample	Treatment	Dose, mrad	Irrad. temp. (°C.)	Wt. Gain, percent
9A.....	15% aqueous acrylic acid; 2 hr., 25° C.	1	25	23.1
9B.....	10% aqueous acrylic acid; 2 hrs., 25° C.	1	25	25.0
9C.....	8% aqueous acrylic acid; 2 hrs., 25° C.	1	25	12.4
9D.....	10% aqueous acrylic acid; 1 hr., 25° C.	1	25	14.0
9E.....	15% aqueous acrylic acid; 1 hr., 25° C.	1	25	11.0
9F.....	50% acrylic acid in toluene; 5 days, 25° C.	1	25	21.8
9G.....	9% aqueous sodium styrene sulfonate; 10 min., 60° C.	2	60	11.8
9H.....	22% aqueous methacrylic acid; 2 hrs., 25° C.	1	25	58.5
9I.....	9% aqueous sodium styrene sulfonate; 10 min., 60° C.	1	60	21.0
9J.....	do.	2	60	8.9
9K.....	35% aqueous styrene sulfonic acid; 10 min., 25° C.	1	25	11.0
9L.....	40% aqueous potassium ethylene sulfonate; 10 min., 25° C.	2	25	4.5
9M.....	25% dist. styrene, 25% maleic acid, 50% CH ₃ OH; 15 min., 25° C.	2	25	2.2
9N.....	15% aqueous acrylic acid; 15 min., 25° C.	1	25	15.0

After irradiation, ungrafted acid is removed by washing four times in distilled water at 80° C. After drying, the weight gain is determined. The fibers show no evidence of surface polymer, and are not bonded to one another.

The acid-grafted samples are then dyed with basic dyes; deeper shades and more rapid dyeing is observed, as compared to an ungrafted control. Sample 9H is heavily weighted, but the fabric hand and appearance are unchanged.

The acid grafted polymer substrates are converted to the sodium salt form by heating in 1% aqueous Na₂CO₃ for 1 hour at 60° C. The property changes obtained are given in Table 5.

TABLE 5

Sample	Property changes	Log R, test vs. control
9A.....	Decreased flammability, increased moisture regain.	ND. ¹
9B.....	do.	ND.
9C.....	do.	ND.
9D.....	Improved resilience, hand; improved resistance to hole melting. ²	9.0 vs. 13.3 8.8 vs. 13.3
9E.....	Improved wickability.	ND.
9F.....	Improved dyeability, printability.	ND.
9G.....	Improved muss and crease resistance, wet.	9.5 vs. 11.7
9H.....	Improved wickability, resistance to hole melting.	7.7 vs. 11.7
9I.....	Improved muss and crease resistance.	7.8 vs. 13.3
9J.....	Improved wickability and wet muss resistance.	7.8 vs. >13.3
9K.....	42% increased water absorption decreased soiling.	ND.
9L.....	Improved hand, like combed cotton.	ND.
9M.....	Increased amount grafted over styrene or maleic acid alone.	ND.

¹ ND indicates properties not determined.

² Resistance to hole melting is estimated by scattering hot ashes from a burning cigarette onto the fabric.

EXAMPLE 10

Pieces of scrubbed cotton sheeting (80 x 80 count) and scrubbed rayon challis are immersed in aqueous solutions of N-methylolacrylamide (MAA) at room temperature, and squeezed between rubber rolls to remove excess solution. The soaking and squeezing are repeated. The amount of N-methylolacrylamide padded on the fabrics is calculated from the wet-pickup and the pad bath concentration. A few fabrics are sealed in polyethylene bags while wet but in most cases fabrics are air-dried prior to sealing. The fabrics in polyethylene bags are exposed at about 25° C. to β -radiation from the 2 mev. vertical Van de Graaff Electrostatic Generator. After irradiation the fabrics are rinsed several times in distilled water, in water containing 0.2% Duponol ME¹ at 50° C. for 30 minutes,

¹ The sodium salt of technical lauryl alcohol sulfate.

and finally in distilled water. The amounts of MAA grafted are determined by weight gains (dried at 110° C. for 1 hour) or from microKjeldahl nitrogen analyses. The data are summarized in Table 6 below:

TABLE 6

Sample	Fabric	Percent MAA in pad bath	Radiated wet or dry	Radiation dose, mrad	Percent gain
10A.....	Cotton.....	3.3	D	2	2.9
10B.....	do.	5	D	2	4.0
10C.....	do.	10	D	2	9.4
10D.....	do.	15	D	2	14.4
10E.....	do.	10.3	W	2	10.6
10F.....	do.	10.3	W	15	14.2
10G.....	Rayon.....	10	D	0	-0.6
10H.....	do.	10	D	2	11.4
10I.....	do.	10	W	2	10.2

To develop improved crease recovery and resilience (fabric "bounce"), the fabrics containing grafted N-methylolacrylamide are soaked in a one percent aqueous solution of tartaric acid and squeezed between rubber rolls. Fabrics are cured, after air drying, at 160° C. for 5 minutes, and are then rinsed well in distilled water. Crease recovery and tensile strength data are summarized in the following table. Data from conventional dimethylolethylene urea (DMEU) treatment are included for comparison.

TABLE 7

Sample	Percent MAA grafted	Before acid treatment crease angle (degrees)	After acid treatment crease angle (degrees)
Cotton sheeting:			
Control.....	0	168	192
10A.....	2.9	151	251
10B.....	4.9	154	268
10C.....	9.4	160	268
10D.....	14.4	154	268
10I.....	4% DMEU	154	250
Rayon challis:			
10G.....	0	217	235
10I.....	10.2	213	235
10H.....	11.4	213	233

Comparisons of cotton fabric properties produced by curing grafted N-methylolacrylamide (MAA) fabrics and dimethylolethylene urea (DMEU) applied in the conventional way are given in Table 8, rated subjectively.

TABLE 8

Sample	Cotton	Monsanto crease angle (degrees)	Fabric bounce	Stability to acid*
Untreated.....		160	Poor.....	
10I.....	DMEU (4% wt. gain).	250	Good.....	Poor.
10B.....	MAA (4.9% wt. gain).	251	Very good.....	Good.

* Acid stability of finish estimated by boiling in 0.2% acetic acid and then comparing swelling and solubility of fibers in cuprammonium solution

It is apparent that at approximately the same weight gain, the fabrics treated in accordance with this invention not only have crease recovery equivalent to conventional dimethylolethylene urea treatments, but show improved fabric "bounce" or resilience, as well as improved stability to acid. Increased amounts of grafted, cured N-methylolacrylamide give some additional improvement. The amount of grafted N-methylolacrylamide required for improving crease-resistance on cellulose is about 2 to 5%, although as much as 15% can be used.

EXAMPLE 11

Increased efficiency of grafting is often obtainable by pretreating the filamentary substrate with a swelling agent for said substrate, or alternatively, dissolving the organic modifier in a solvent which has a pronounced swelling action for the fiber. This example illustrates the advantages.

A switch of rayon taffeta woven from 100 denier 40 filament rayon is soaked in a solution consisting of 10

ml. of methanol and 10 ml. of diallyl itaconate for a period of about 1 hour. Excess liquid is squeezed from the fabric sample by passing it through a wringer, the sample is then wrapped in aluminum foil and exposed to a dose of 2 mrad of electrons from a 2 mev. electron accelerator. After irradiation, the sample is washed for 30 minutes in hot methanol, followed by rinsing three times in an agitation washer containing water at 70° C. The sample is then dried; a weight gain of 1.5% is observed. The sample is much more dyeable with basic dyes, compared to an untreated, non-irradiated control.

When the test is repeated with another swatch of the same fabric, the only change being that the sample is immersed in pure diallyl itaconate without the methanol swelling agent, a weight gain less than 0.1% is observed.

TEXTILE SUBSTRATE

As illustrated in the examples, the textile produced from the fiber-forming, carbonaceous polymer of nature acts as a substrate to which the organic compound is bonded by means of radiation.

The textiles treated in accordance with this invention include natural fibers such as cotton, flax, jute, hemp, ramie, sisal, abaca, phormium, silk, wool, fur, hair and materials produced from derivative and regenerated forms of natural polymers, such as cellulose acetate, cellulose triacetate, regenerated cellulose, protein fiber derived from peanut protein, zein, casein and the like. Indeed, film such as regenerated cellulose or natural rubber film may be treated in accordance with the process of this invention, and thereafter be slit to form fine ribbon-like filaments useful for making fabrics, etc. The process of the present invention may be applied to a funicular structure such as a continuous fiber, a filament, a spun yarn, cord, tow, floc, bristle, artificial straw, staple or the like. It may likewise be applied to a fabric of a woven, knitted, felted or other construction.

The shaped article, where its nature will permit, such as in cellulose acetate, may be in the form of finely comminuted particles which may, after having the organic compound grafted to it, be dissolved and shaped by dry spinning into a fiber. However, since the grafted natural polymer must be soluble or melt-spinnable the versatility of this embodiment of the process is limited; thus, it is preferred to perform the grafting operation on the polymer in its final shape, e.g., in textile form. In this way, the location of the grafted modification may be controlled, whether upon the surface, partially penetrating the filament, or completely penetrating it, effecting a "bulk" modification.

OPERABLE MODIFIERS

Any organic compound may be employed as the modifying material which may be grafted to the textile. By an "organic compound" is meant a material having the formula CX_4 where the subscript 4 indicates the total valence bonds available for the X substituents and where X is a member of the group consisting of hydrogen, halogen, nitrogen, nitrogen radical, oxygen, oxygen radical, sulfur, sulfur radical or organic radical linked to the CX residue by a carbon-to-carbon bond. Furthermore, the C may be doubly bonded to no more than one S= or O= atom; i.e., only one pair of X's may be replaced by a divalent oxygen or sulfur atom. Compounds with aliphatic unsaturation are especially preferred since a minimum radiation dose is required to graft a given weight of modifier.

UNSATURATED MODIFIERS

Among suitable materials are hydrocarbons such as ethylene, propylene, styrene, α -methyl styrene, divinyl benzene, 1,3-butadiene, 2,3-dimethyl-1,3-butadiene, 2-chloro-2-, 3-butadiene, isoprene, cyclopentadiene, chloroprene; acids such as maleic acid, crotonic acid, dichloromaleic acid, furoic acid, acrylic acid, methacrylic acid, undecylenic

acid, cinnamic acid; amides such as acrylamide, methacrylamide, N-methylacrylamide, N-methyl, N-vinyl formamide, N-vinyl pyrrolidone, methyl substituted N-vinyl pyrrolidone, vinyl oxyethyl formamide, methylene-bis-acrylamide, N-allyl-caprolactam; acrylate esters such as methyl acrylate, ethyl acrylate, benzyl acrylate, octyl acrylate, methyl methacrylate, butyl methacrylate, vinyl acrylate, allyl acrylate, ethylene diacrylate, diallyl itaconate, diethyl maleate, N,N-diethylaminoethyl methacrylate, dihydroxy dipyrone; nitriles such as acrylonitrile, methacrylonitrile; acrylyl halides such as acrylyl chloride; vinylic alcohols such as allyl alcohol, furfuryl alcohol, 3-hydroxycyclopentene, dicyclopentenyl alcohol; tropolone; aldehydic compounds such as acrolein, methacrolein, crotonaldehyde, furfural, acrolein diethyl acetal; vinyl amines such as vinyl pyridine, allyl amine, diallyl amine, vinyloxyethylamine, 3,3-dimethyl-4-dimethylamino-1-butene, N,N-diacryltetramethylene diamine, N,N-diallyl melamine, diamino octadiene; quaternized amines such as tetraallyl ammonium bromide, vinyl trimethyl ammonium iodide, the quaternary methiodide of methylene-3-aminomethylcyclobutane; vinyl esters such as vinyl acetate, vinyl salicylate, vinyl stearate, allyl formate, allyl acetate, diallyl adipate, diallyl isophthalate; vinyl ethers such as allyl glycidyl ether, vinyl 2-chloroethyl ether, dihydropyran, methoxy polyethyleneoxymethacrylate; vinyl chloride, vinyl fluoride, tetrachloroethylene, tetrafluoroethylene, 1,1-dichloro-2,2-difluoroethylene, vinylidene chloride, hexachloropropene, hexachlorocyclopentadiene, p-chlorostyrene, 2,5-dichlorostyrene, allyl bromide, 2-bromoethyl acrylate, vinyl tetrafluoropropionate, 1,1,7-trihydroperfluoroalkylacrylate such as 1,1,7-trihydroperfluoroheptylacrylate; isocyanate type compounds such as vinyl isocyanate, acrylyl isocyanate, allyl isothiocyanate; vinyl ketones such as methyl vinyl ketone, ethyl vinyl ketone; cyanides such as methacrylyl cyanide, allyl isocyanide; nitro compounds such as 2-nitropropene, 2-nitro-1-butene; phosphorous containing vinyls such as diethyl vinyl phosphate, diphenyl vinyl phosphine oxide, 1-phenyl-3-phosphacyclopentene-1-oxide, diallyl benzene phosphonate, potassium vinyl phosphonate, bis-chloroethyl vinyl phosphonate; also included are alkyl, aryl, aralkyl phosphonates, phosphites and phosphonates; sulfur containing vinyls including sulfonates, sulfonamides, sulfones, sulfonyl halides; thiocarboxylates, such as diallyl sulfide, ethylene sulfonic acid, allyl sulfonic acid, methyl allyl sulfonic acid, styrene sulfonic acid, 2-methylpropene-1,3-disulfonic acid, also including salts and esters of the sulfonic acids; epoxy vinyls, such as butadiene oxide, glycidyl methacrylate.

Acetylenes such as phenylacetylene, acetylene dicarboxylic acid, propiolic acid, propargylsuccinic acid, propargyl alcohol, 2-methyl-3-butyne-2-ol, 2,2,3,3-tetrafluorocyclobutylvinylethylene and the like may be used successfully.

NON-POLYMERIZABLE MODIFIERS

In addition to compounds containing ethylenic unsaturation, it has been found that compounds can be grafted, according to the process of this invention, which are ordinarily regarded as non-polymerizable. By non-polymerizable is meant those compounds, free from aliphatic unsaturation, which do not polymerize by free radical initiation. Due to the efficiency of the high-energy radiation in producing free radicals, it is theorized that free radicals are produced simultaneously on the polymer substrates and on the saturated non-polymerizable compounds, whereupon grafting ensues. The preferred non-polymerizable compounds are those which have functional groups which are useful in modifying polymer properties. Thus, such compounds are included as hydrocarbons, alcohols, acids, ethers, ketones, esters, aldehydes, isocyanates, sulfonates, mercaptans, thioethers, disulfides, nitriles, nitro compounds, amines, amides and halides. Typical of suitable alcohols are the alkanols such

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as methanol, ethanol, laur^{ol}, the polyols, such as glycerine, pentaerthritol, sorbitol, mannitol, their partial esters and the like. Dialkyl ethers such as dimethyl, diethyl, ethylmethyl and the glycol ethers as well as the oxalkylated ethers of partial esters of the polyols, such as the polyoxyethylene derivative of a fatty acid partial ester of sorbitol are suitable. Oxides such as 1,2-diisobutylene oxide are useful. Mercaptans and thioethers analogous to the above may be used as may also disulfides of a similar nature. As amines may be mentioned the alkyl amines such as methyl amine, ethyl amine, hexamethylene diamine and dodecylamine. The amides of these amines formed with acids such as formic acid, adipic acid, suberic acid, stearic acid and the like are useful; alternatively, the acids alone are often desirable modifiers. Halides within the preferred class include the alkyl halides such as chloromethane, chloroform, carbon tetrachloride, chloroethane, chloroethylene, dichlorodifluoromethane, dodecafluoroheptyl alcohol and similar materials.

Of the non-polymerizable compounds, those organic compounds, the bonds of which are easily broken, as, for instance, chain transfer agents, are particularly preferred, since larger amounts of modifier are grafted with a given irradiation dose.

It is, of course, obvious that low molecular weight non-polymerizable modifiers are preferred, when it is desirable to have the modifier penetrate into the polymer substrate, to make a bulk modification. It has been observed that modifiers with functional groups which have a swelling effect upon the polymer substrate are usually especially effective in penetrating the substrate.

POLYMERIC MODIFIERS

Polymeric modifiers are a preferred class for grafting to substrates which are in the form of fibers, filaments, fabric or the like. These modifiers are especially suitable when a surface coating is desired, since it is obvious that their ability to penetrate will be limited. When irradiating these compositions, it is believed that the coating is grafted by chemical bonds, probably carbon-carbon bonds, to the fiber surface. Therefore, the process of this invention gives a much more durable coating than those obtainable by prior art processes which require polymerization initiators to cross-link the coating, and depend on mere physical bonds to retain the coating upon the textile. The polymeric modifiers are especially adaptable to the process of this invention, since relatively few bonds are needed to graft each large macromolecule to the fiber surface.

The process of this invention is especially suitable for washfast modification of fibers and fabrics, as has been shown by the examples hereinabove. These advantages are obtained by selecting polymeric modifiers which can be applied in a relatively fluid state, e.g., from solution emulsion or as a melt. Viscosities up to about 100 centipoises may be employed, but lower viscosities are preferred. When these conditions are met the modifier migrates into the yarn bundles so that each filament in the fabric is individually coated, and a large excess of the modifier is avoided. Excess amounts of modifier result in a deleterious effect on fabric hand, and often render the fabric unfit for apparel use. The preferred polymeric modifiers are those which are soluble or dispersible in aqueous solutions, al though other solvents may be used in some cases. However, water is the preferred solvent because of its cheapness, availability, and freedom from hazards. Thus, such polymers are preferred as the polyether glycols, polypropylene ethers, polymeric alcohols, polymeric acids, polymeric amines, polymeric amides and the like. These compounds are useful, for example, in increasing moisture regain, antistatic effect, and wickability, even beyond that which is characteristic of natural polymers. Alternatively, water repellence can be improved by grafting hydrophobic polymeric materials, usually utilizing a solvent other than water. Examples of such hydro-

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phobic polymers are polytetrafluoroethylene, polyvinyl chloride, polymeric esters and the like.

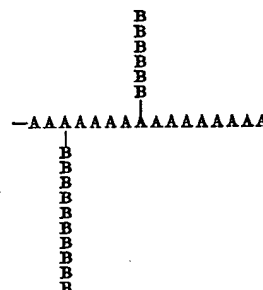
STRUCTURE OF GRAFT COPOLYMER PRODUCT

5 The process of this invention produces a polymeric structure which has been termed a graft copolymer, that is, a polymer in which modifying agent (monomer, organic compound, or other polymeric chain), is grafted by
10 chemical bonds, usually as a side chain, to the parent polymeric substrate.

Conventional copolymers, consisting of monomer species A and B, have a random distribution along the backbone of the polymer molecule, and may be represented schematically thus:

—AAABBABBBABAA—

The graft copolymer species with which this invention is concerned, consists of a main chain of polymer A, and side chains of polymer B grafted thereto, represented below:



The characteristic of this copolymer type is that its gross properties remain predominantly those of the polymer (A) forming the molecular backbone. However, modifications can be produced via polymer (B) grafts, in most cases, without loss of the original desirable properties. As an example, conventional copolymers usually have a lower melting point than those of either component, while graft copolymers usually retain the high melting point of the pure backbone component. The structure and preparation of some examples of these copolymer types is discussed in a comprehensive review article by E. H. Immergut and H. Mark in *Macromolekulare Chemie* 18/19, 322-341 (1956).

The organic compound modifier may be applied to the carbonaceous natural textile by immersion, padding, calendering, spraying, exposure to vapor condensation, or by other similar means. Usually, it will be desirable to remove excess liquid by squeezing, centrifuging or blotting prior to exposure to irradiation, thus preventing excess surface deposits which might bond the filaments together. Alternatively, the organic modifier may be deposited on the textile by flashing off the solvent in which it is dissolved prior to application.

As described previously, it is desirable that the modifier be applied to the substrate in a highly fluid condition; thus, application from solutions with a viscosity of the same order of magnitude as water are preferred. This permits completely coating each fiber of filamentous substrates.

The process of the instant invention is directed to producing modifications throughout the bulk of the polymer substrate only when the modifier, applied to the surface, penetrates therethrough; for modifiers which do not penetrate, modification is restricted to the surface.

70 Thus, when the polymer is penetrated with the modifier prior to initiating the graft polymerization, modification of the shaped structure extends at least through a substantial proportion of the body of the final product.

Increased contact time and agitation are helpful in increasing penetration. It is sometimes beneficial to carry out the soaking for penetration at elevated temperatures

at super-atmospheric pressure or in the presence of swelling agents, dye carriers, or the like. However, elevated temperatures are to be avoided when using modifiers, such as strong acids, which may degrade hydrolysis-susceptible polymers. Minor amounts of wetting agents, surface active compounds, and the like are useful for improving penetration efficiency.

When it is desirable to limit penetration of a diffusible modifier to a zone near the fiber surface, this may be accomplished by reduced contact time or temperature, or the use of modifiers with greater chain length. Alternatively, the fiber may be exposed to the modifier for the time required to effect the desired penetration, then penetration may be stopped by freezing, for example with Dry Ice. The combination may then be irradiated while frozen, and grafting will occur when the combination is warmed.

Where the modifier is applied from a solution, water is usually the preferred solvent. Other inert liquids are suitable for this purpose, however, such as alcohol, benzene, toluene, glycol, high boiling ethers and the like; where high soaking or irradiation temperatures are used, a non-volatile solvent is often advantageous.

RADIATION WHICH IS EFFECTIVE

The ionizing radiation useful in the process of this invention must have at least sufficient energy to non-selectively break chemical bonds. This radiation is to be distinguished from ultraviolet radiation, which is effective in activating or ionizing only specific chemical bonds; such bonds are responsive to ultraviolet radiation only of given wave lengths. It is often necessary to use an ultraviolet photo-initiator in such reactions, so that light of available wave lengths will initiate the desired chemical reaction. In contrast, the ionizing radiation of this invention has sufficient energy so that it exceeds that which is required to break any chemical bond. Thus, this ionizing radiation serves to activate polymer substrates so that chemical reactions are initiated with any organic compound, or, alternatively, to activate non-polymerizable organic compounds so they react with the polymer substrate.

In general, ionizing radiation is preferred which has sufficient energy so that appreciable substrate thickness is penetrated, and in addition radiation absorption by the atmosphere is sufficiently low so that it is unnecessary to operate in a vacuum. Such radiation has energy of at least 0.1 mev. Higher energies are even more effective; the only known upper limit is imposed by available equipment.

The ionizing radiation of the process of this invention is generally considered in two classes: particle radiation, electromagnetic radiation. Effects produced by these two types of radiation are similar, since in their interaction with matter, each generates secondary radiation of the other type. The important consideration is that the incident radiation exceed a minimum threshold energy. Details of the mechanism of the interaction of high energy electrons with organic matter, including polymers, are not completely known but the initial reaction is considered to be the absorption of energy by the valence electrons of the irradiated molecules in or near the path of the high energy electrons. The absorbed energy may be so great that some valence electrons will be shot off fast enough to ionize still other molecules. Some of the displaced electrons fall back to form neutral molecules and give up their energy as electromagnetic radiation, which in turn can be absorbed by other molecules and thus raise them to an excited stage. Further redistribution of the energy in the molecules results primarily in C—C bonds splitting off H atoms or molecules, producing free radicals or unsaturation.

The similarity of effect between the two types of radiation is thought to be due to the fact that an electron is ejected when an atom absorbs a quantum of high energy X- or gamma-rays; the electron has sufficient energy so

that it in turn ejects electrons from other atoms, corresponding in effect to irradiation with an electron beam. Thus, the initial effect of high energy irradiation is to produce high energy electrons, which within the irradiated substrate produce free radicals. Consequently, the effects produced by particle and electromagnetic irradiation of equivalent energy are very similar, and differ only in the rate at which the effect is produced, which is a function of dose rate. The dose rate is a function of the equipment available to produce it, rather than an inherent limitation of the type of irradiation. Thus, with present day equipment, higher dose rates are obtainable with electron irradiation than are obtainable with X-rays of equivalent energy.

Although the fundamental particles differ from one another in size and charge, their mechanism or energy loss is essentially the same. Thus, their effect on chemical reactions is also similar. Although the neutron is not a charged particle, it, however, produces protons and gamma-rays which lose energy in the normal ways and consequently is effective in the process of this invention.

Therefore, the high energy particle radiation effective in the process of this invention is an emission of highly accelerated electrons or nuclear particles such as protons, neutrons, alpha particles, deuterons, beta particles, or the like, directed so that the said particle impinges upon the textile bearing the organic compound. The charged particles may be accelerated by means of a suitable voltage gradient, preferably at least 0.1 mev., using such devices as a resonant cavity accelerator, a Van de Graaff generator, a betatron, a synchrotron, cyclotron or the like, as is well known to those skilled in the art. Neutron radiation may be produced by bombardment of selected light metal (e.g. beryllium) targets. In addition, particle radiation suitable for carrying out the process of the invention may be obtained from an atomic pile, or from radioactive isotopes or from other natural or artificial radioactive materials.

Similarly, ionizing electromagnetic radiation useful in the process of this invention is produced when a metal target (e.g., gold or tungsten) is bombarded by electrons possessing appropriate energy. Such energy is imparted to electrons by accelerating potentials in excess of 0.1 million electron volts (mev.). Such radiation, conventionally termed X-ray, will have a short wave length limit of about 0.01 angstrom units (in the case of 1 mev.) and a spectral distribution of energy at longer wave lengths determined by the target material and the applied voltage. X-rays of wave lengths longer than 1 or 2 angstrom units are attenuated in air thereby placing a practical long wave length limit on the radiation. In addition to X-rays produced as indicated above, ionizing electromagnetic radiation suitable for carrying out the process of the invention may be obtained from a nuclear reactor ("pile") or from natural or artificial radioactive material, for example, cobalt 60. In all of these latter cases the radiation is conventionally termed gamma-rays. While gamma radiation is distinguished from X-radiation only with reference to its origin, it may be noted that the spectral distribution of X-rays is different from that of gamma-rays, the latter frequently being essentially monochromatic, which is never the case with X-rays produced by electron bombardment of a target.

RADIATION ENERGY

To be efficient in the practice of the present invention, it is necessary that the high energy particles have sufficient velocities to permit penetration of several layers of material, when fabrics or films are being treated. Although an energy of about 50 ev. is enough to initiate the grafting reaction, energies of at least 0.1 mev. are preferred, for efficient penetration. The velocity required will depend on the nature of the particle and also on the nature of the substrate to a certain extent. An electron which is accelerated by a potential of a million volts

(mev.) will effectively penetrate a thickness of polyhexamethylene adipamide fabric of about 0.25 cm. A more universal measure of penetration for all substrates is in units of grams penetrated per square centimeter irradiated. Thus, 2 mev. electrons will effectively penetrate 0.7 gm./cm.² of any shaped article, while 1 mev. electrons are effective for 0.35 gm./cm.².

As stated previously, there is no known upper limit to the particle energy, except that imposed by present day equipment. Thus, energies equivalent to 24 mev. to 100 mev. may be used.

As a guide in using other charged particles which have been shown to be effective in grafting the table below shows particle energies required to give penetration equivalent to 0.1 mev. electrons.

Particle:	Accelerating potential, mev.
Electron, e ⁻ -----	0.1
Proton, H ⁺ -----	3.0
Deuteron, D ⁺ -----	4.0
Alpha, He ⁺⁺ -----	12.0

It should be recognized that the heavier charged particles are especially adapted to creating surface effects, due to their lower penetration at a given energy. In situations where surface effects are paramount, it is not necessary that the shaped article be completely penetrated by the high energy particle and lower accelerations may be employed. Under those conditions, if the surface effect is to be applied to both sides of the shaped article, it will obviously be necessary to expose each of the surfaces to the particle radiation. This is done by simultaneously bombarding both sides of the shaped article or alternatively by subjecting each side to the single source of irradiation during different runs.

High energy particle radiation has special utility for grafting modifiers to thin substrates, e.g., fabrics, filaments and films. The required irradiation doses with present day electron accelerators, such as exemplified herein, are attained rapidly, in a matter of seconds, thus promoting a high rate of throughput.

In comparison, high energy electromagnetic radiation in short wave lengths is highly penetrating, and hence readily lends itself to treating massive substrates. When grafting to the preferred substrates of this invention, this type of radiation is especially useful for irradiating materials present in multiple layers. For example, rolls of film, bolts of fabric, yarn packages, bales of staple fiber, or the like, may be irradiated as a single unit.

As an illustration, X-rays generated by electrons of 2 mev. have adequate penetration for polymer samples of several inches in thickness. Lower energy (longer wave length) X-rays are, of course, less penetrating, so that it may be necessary to reduce the thickness of material to be treated simultaneously. In addition, the very long (soft) X-rays, because of low penetration, may be especially effective in producing surface effects.

Although the treatment can be carried out using conventional X-ray equipment, the use of radioactive isotopes such as cobalt 60 is especially economical. Radiation from waste fission products, with particle irradiation screened off if desired, is also effective and offers an opportunity to utilize an otherwise useless waste product.

RADIATION DOSE

In determining the optimum dose of irradiation for any particular combination, both the nature of the organic compound and the nature of the solid substrate must be considered. For example, for vinyl monomers which are readily graftable, and polymer substrates that are readily activated by ionizing radiation, it appears that the greater part of the minimum irradiation dose is required to consume the inhibitor (including oxygen) which may be present in the vinyl monomer. After that is done, relatively low additional doses will produce enough radicals to initiate graft polymerization. For readily graftable

combinations of this type, a high propagation constant is observed. Thus, the extent of irradiation-induced graft polymerization can be increased by increasing either radiation dose, post-irradiation time, post-irradiation temperature, or all three. For instance, if a polymer soaked in acrylic acid solution is irradiated with a dose of 0.06 mrad, and the irradiated sample is kept in contact with the acrylic acid solution for 1 hour at room temperature, a large amount of the acid is grafted. In contrast, with the same dose, if monomer is removed from the sample immediately after irradiation (e.g., by a water extraction), only one-third as much acrylic acid is grafted. Therefore, for polymerizable vinyl compounds and readily graftable polymer substrates, a very small dose is required; thus, a minimum dose of 5000 rads (0.005 mrad) initiates a significant amount of grafting.

When unsaturated compounds which are not homopolymerizable (e.g., maleic acid) are used as the modifier, in combination with readily graftable substrates, doses of 0.1 mrad are required to initiate appreciable grafting. When non-polymerizable organic compounds or saturated polymeric modifiers are used, a minimum dose of 1 mrad should be employed. Radiation doses below the minimum specified fail to initiate beneficial amounts of grafting within a practical length of time. This is due to the fact that the life of free radicals produced by the irradiation depends on a balance between competing (i.e., non-grafting) reactions and those which produce grafting. It is obvious, of course, that even lower doses may be used in completely inhibitor- and oxygen-free systems, or if irradiation-initiation of grafting is supplemented by a chemical initiator.

Although the minimum doses specified are effective, higher dosages may be used and are usually highly beneficial. Dosages so high that substantial degradation of the shaped substrate occurs must obviously be avoided. High doses crosslink some polymers, which may sometimes be undesirable.

As a guide in this regard, wool fiber may be irradiated to a dosage as high as 80 mrad. However, it is preferred that the dosage applied to these substrates not exceed about 60 mrad. An upper limit of about 40 mrad is suggested for silk, while cellulose fiber substrates are preferably subjected to no more than 20 mrad.

REACTION CONDITIONS

Once free radicals are produced on the carbon atoms of the polymer chain in the presence of a vinyl monomer, vinyl polymerization is initiated, and polyvinyl chains grow from the initiating site.

However, it has been observed that the life of free radicals is many times greater than has been found in vinyl polymerizations carried out in solution or emulsions. For this reason, at a given radiation dose, the yield of polymer grafted to the shaped substrate is much greater than would be obtained, for example, if the substrate polymer were dissolved in the vinyl monomer and the solution irradiated.

The average molecular weight of the grafted polymer chains (at a given constant weight gain) may be controlled by adjusting the radiation dose. It may also be adjusted by controlling chain transfer to the substrate polymer, e.g., by changing grafting temperatures, or modifying the substrate polymer by incorporating copolymer components which are more (or less) susceptible to chain transfer. Similarly, the molecular weight distribution of the grafted polymer chains may be adjusted. By controlling the number, length and length distribution of grafted chains, the effect produced by a given grafting agent may be modified.

It has been observed that irradiation of the modifier-treated textile in the presence of air or moisture may occasionally cause some degradation; such adverse effects can be avoided by employing an atmosphere of inert gas around the article while it is being irradiated. Alterna-

tively; a satisfactory and simpler approach is to wrap the sample in a material which is substantially air and water impervious, thus limiting the quantity of air or moisture contacting the sample. Complete exclusion of oxygen is not required, although it may contribute to grafting efficiency when using a vinyl monomer. In some of the examples, the samples are wrapped in polyethylene film. Aluminum foil is satisfactory. The nature of such wrapping material is not critical, provided it is substantially impervious to air and moisture, when required, and is readily penetrated by the radiation.

IRRADIATION CONDITIONS

In the process of this invention it may be desirable to include in the combination to be irradiated, materials which may have a protective or antioxidant effect in preventing radiation degradation of either modifier or substrate or both. Compounds of this type are cysteine, carbon, polyethylene glycols and the like. It may also be desirable to include in the combination to be irradiated materials which absorb radiation and transmit the energy thus absorbed to the modifier or the organic polymeric material or both, whereby adhering is promoted and the efficiency of utilization of the radiation is increased. Compounds with this property are somewhat similar to sensitizers in photography, except that in this case useful materials absorb high energy radiation and emit the energy in a lower or more usable range. Phosphor screens containing calcium tungstate, zinc sulfide or metallic lead or the like have utility for this purpose. The phosphor materials may be used as plates contacting the material being treated, or may be incorporated in the modifying agent or even be coated on or dispersed in the organic polymeric material which it is desired to modify.

The irradiation may be accomplished over a wide range of temperatures. However, a low temperature decreases the tendency toward oxidation. Since the absorption of particle radiation frequently causes a temperature increase in the range of about 2° C. for each mrad absorbed, if high tube current is employed so that radiation absorption is complete within a short time interval, it is usually advisable to provide means to remove the heat generated to avoid injury to the sample. The use of Dry Ice to maintain a cold atmosphere is very satisfactory for this purpose. In general, irradiation at a higher temperature promotes the speed with which bonding occurs, thus promoting a higher throughput of a given piece of equipment at a constant radiation dosage. Temperatures ranging from -80° C. or below up to the melting point of the polymer substrate may be employed. More efficient grafting is often noted when irradiation temperatures are in the range of 100 to 160° C.

In general, the greatest weight of modifier is grafted for a given dose when the organic compounds are applied to the substrate as liquids or concentrated solutions. However, this finding must be followed with caution, since the "fabric" character must be preserved. In many instances, unless excess solution is removed from the textile prior to irradiation, large amounts of homopolymer may be formed on the surface of the filaments, bonding them together in a stiff, unattractive mass. This not only represents a loss of modifier, but, if not removed, will render the textile unfit for apparel use. In order to avoid this result, it is recommended that (a) modifier compositions be avoided which cross-link to an insoluble state under irradiation doses needed for grafting; (b) that excess modifier be removed prior to or after grafting.

Prior to treatment, the textile may be oriented by hot or cold drawing. It may contain additives such as pigments, antioxidants, fillers, polymerization catalysts and the like. After the irradiation, the product may be after-treated. Frequently a certain amount of homopolymer formation occurs at the surface which is readily removed by solvent extraction or washing. This treatment is usually preferred. In other after-treatments, the shaped

article may be dyed, bleached, hot or cold drawn, chemically reacted, or given coatings of lubricants, sizes or the like or other similar treatments.

UTILITY

The process of the present invention is valuable in creating both surface and bulk effects upon textiles produced from carbonaceous natural polymers. It may be employed upon textiles to affect softness, resilience, tendency to shrink, static propensity, resistance to holmelting, pilling, hydrophilicity, wickability, and the like. It is useful in changing such properties as tenacity, elongation, modulus, creep, compliance ratio, work recovery, tensile recovery, decay of stress, wet properties, high-temperature properties, abrasion and wear resistance, moisture regain, flex life, hydrolytic stability, heat-setting properties, boil-off shrinkage, dry-cleaning properties, heat stability, light durability, zero strength temperature, melting point, soilability, ease of soil removal, laundering properties, washwear properties, liveliness, crease resistance, crease recovery, torsional properties, hysteresis properties, fiber friction, dyeability (depth rate permanence and uniformity), printability, washfastness of dyes or finishing treatments (resins, ultraviolet absorbers, etc.), handle and drape properties (stiffening or softening), heat-yellowing, snag resistance, elasticity, density, ease in textile processability, solubility (insolubilization or increase in solubility), bleachability, surface reactivity, delustering action, drying properties, fabric life, crimpability, stretchability, fabric stabilization, compressional resilience (rugs), thermal and electrical conductivity, transparency, light transmittance, air and water permeability, fabric comfort, felting, ion exchange properties, germicidal properties, adhesion, over-all appearance and combinations of these as well as other.

It is apparent that those properties which are not primarily a function of surface characteristics of the filament (e.g., tenacity, elongation, modulus, and the like) may be more conveniently modified by using modifiers which penetrate the filaments prior to irradiation-grafting, thus producing a graft copolymer extending throughout the penetrated volume. It is also apparent that at times it may be desirable to allow one or more modifiers to penetrate the filaments, and coat one or more modifiers on the surface of the filaments, then initiate grafting simultaneously by irradiating them.

Although the invention has been described in terms of treating filamentary structures in the form of yarn or woven or knitted fabric, the process is applicable to fabricated textiles for clothing or industrial use, reinforcement for composite structures (such as cords for mechanical rubber goods, fiber for laminates, etc.), bristle or artificial straw, and the like.

Many other modifications will be apparent to those skilled in the art from a reading of the above description without a departure from the inventive concept.

What is claimed is:

1. Method for beneficially modifying substantially pure cellulosic substrates which comprises first contacting the substrate with an aqueous solution, in a substantially neutral pH, of a water-soluble ethylenically unsaturated monomer that is polymerizable in aqueous solution under the influence of a field of ionizing high energy radiation; continuing contact of said substrate with said monomeric solution until the former is at least partially swollen by the latter; then subsequently exposing the cellulosic substrate while it is in contact with the aqueous monomeric solution to a field of ionizing high energy radiation until at least the surface of the substrate has become modified with the saturated reaction product of said monomeric material that has been chemically reacted to provide said reaction product in the presence of and in intimate association with said substrate.

2. The method of claim 1, wherein the substrate is comprised of cotton fibers.

3. The method of claim 1, wherein the substrate is comprised of regenerated cellulose.

4. The method of claim 1, wherein the substrate is comprised of viscose rayon fibers.

5. The method of claim 1, wherein the field of ionizing high energy irradiation that is employed for the modifying reaction has an intensity of at least about 40,000 roentgens per hour.

6. The method of claim 1, wherein the amount of water-soluble monomer in aqueous solution that is in contact with said substrate is an amount of the monomer between about 1 and 40 percent by weight, based on the weight of the substrate.

7. The method of claim 1, wherein the amount of water-soluble monomer in aqueous solution that is in contact with said substrate is an amount of the monomer between about 5 and 20 percent by weight, based on the weight of the substrate.

8. The method of claim 1, wherein said monomer is selected from the group consisting of acrylonitrile, methacrylonitrile, acrylamide, acrylic acid, methyl methacrylate, sulfonated styrene monomers, vinyl lactam monomers and methyl isopropenyl ketone.

9. The method of claim 1, wherein said monomer is a para-sulfonated styrene monomer.

10. The method of claim 1, wherein said monomer is vinyl pyrrolidone.

11. The method of claim 1, wherein said monomer is acrylonitrile.

12. Modifying a cotton fiber substrate with acrylonitrile by a method according to the method set forth in claim 1.

13. Modifying a cotton fiber substrate with N-methylolacrylamide according to the method set forth in claim 1.

14. Method for modifying cellulosic substrates which comprises immersing the substrate in aqueous N-methylolacrylamide until said substrate is at least partially swollen; and subsequently exposing said substrate to a field of ionizing high energy radiation until at least the surface of the substrate has become modified by a chemical reaction in which said acrylamide is grafted to said substrate.

References Cited

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MURRAY TILLMAN, Primary Examiner

R. B. TURER, Assistant Examiner

U.S. Cl. X.R.

260—17, 17.4, 8, 5, 4; 8—116, 116.2, 31, 55, 100, 54, 127.6, 129, 57, 128, 5.10

[54] METHOD OF INCREASING THE WATER ABSORPTION OF CELLULOSE-CONTAINING MATERIALS

[75] Inventors: Joel Lawson Williams, Cary; Vivian Thomas Stannett, Raleigh, both of N.C.

[73] Assignee: Research Corporation, New York, N.Y.

[21] Appl. No.: 665,181

[22] Filed: Mar. 9, 1976

[51] Int. Cl.² D06M 13/20; D06M 13/30; D06M 13/34; D06M 5/24

[52] U.S. Cl. 8/130.1; 8/120; 8/125; 8/131; 8/181; 8/196; 8/DIG. 12; 8/DIG. 18; 260/17.4 GC; 260/17.4 CL

[58] Field of Search 8/125, 130.1, 131, 196, 8/DIG. 18, DIG. 12, 120, 181; 260/17.4 GC, 17.4 CL, 120

[56]

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Primary Examiner—John Kight, III

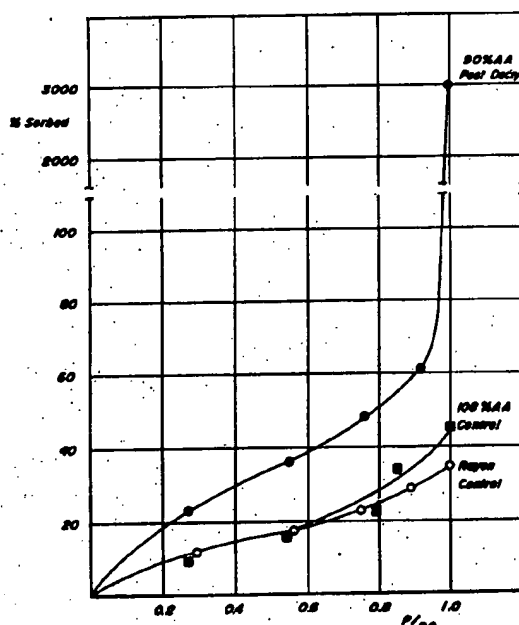
Attorney, Agent, or Firm—Dennis P. Clarke

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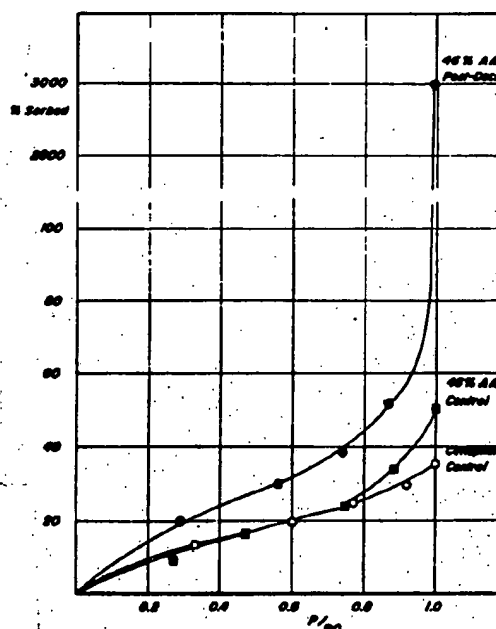
ABSTRACT

A process for increasing the water-absorbency of cellulose-containing materials by graft-copolymerizing onto said material a vinyl monomer containing a hydrophilic group and treating the graft-copolymerized material with a decrystallizing agent for cellulose.

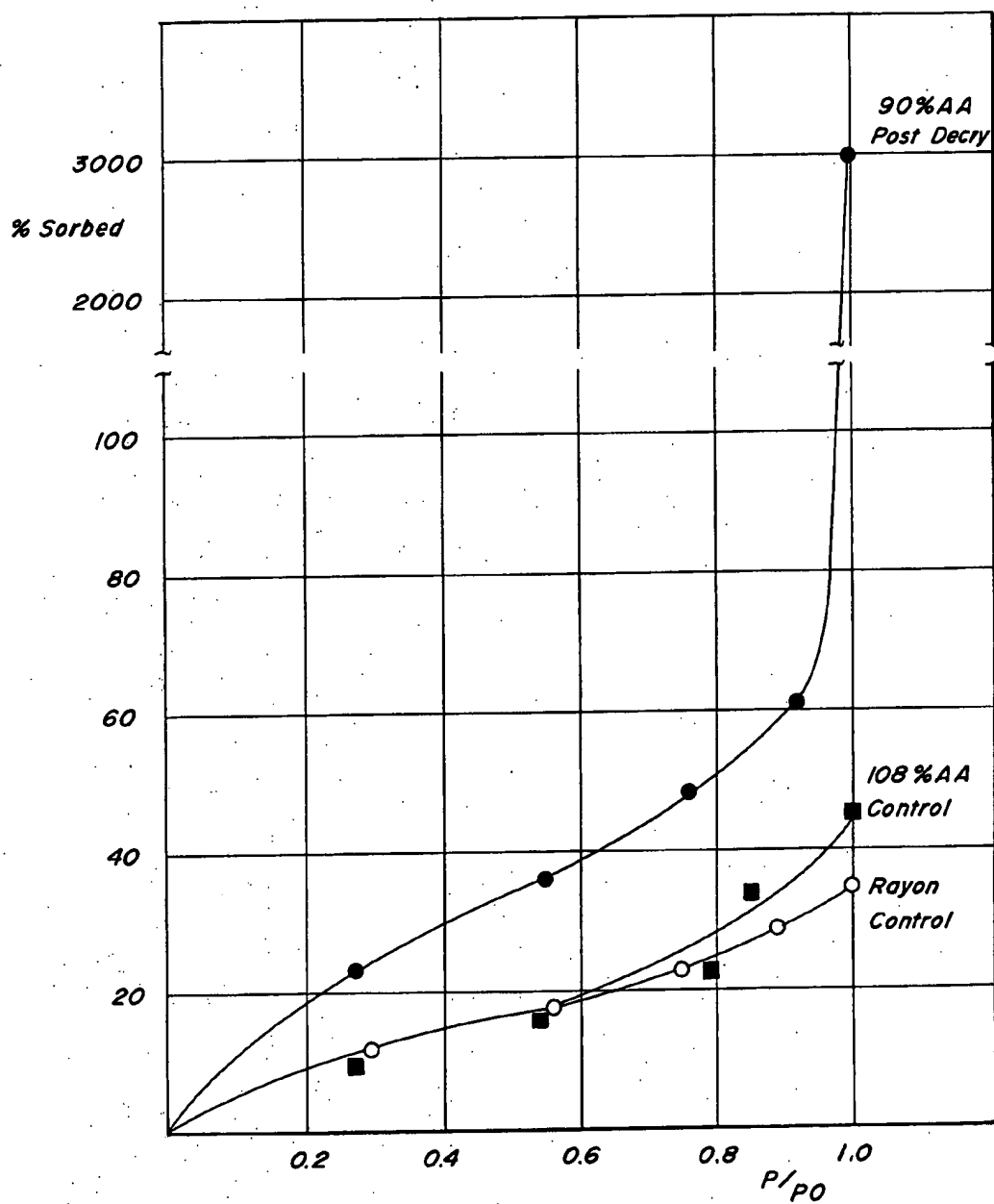
17 Claims, 2 Drawing Figures



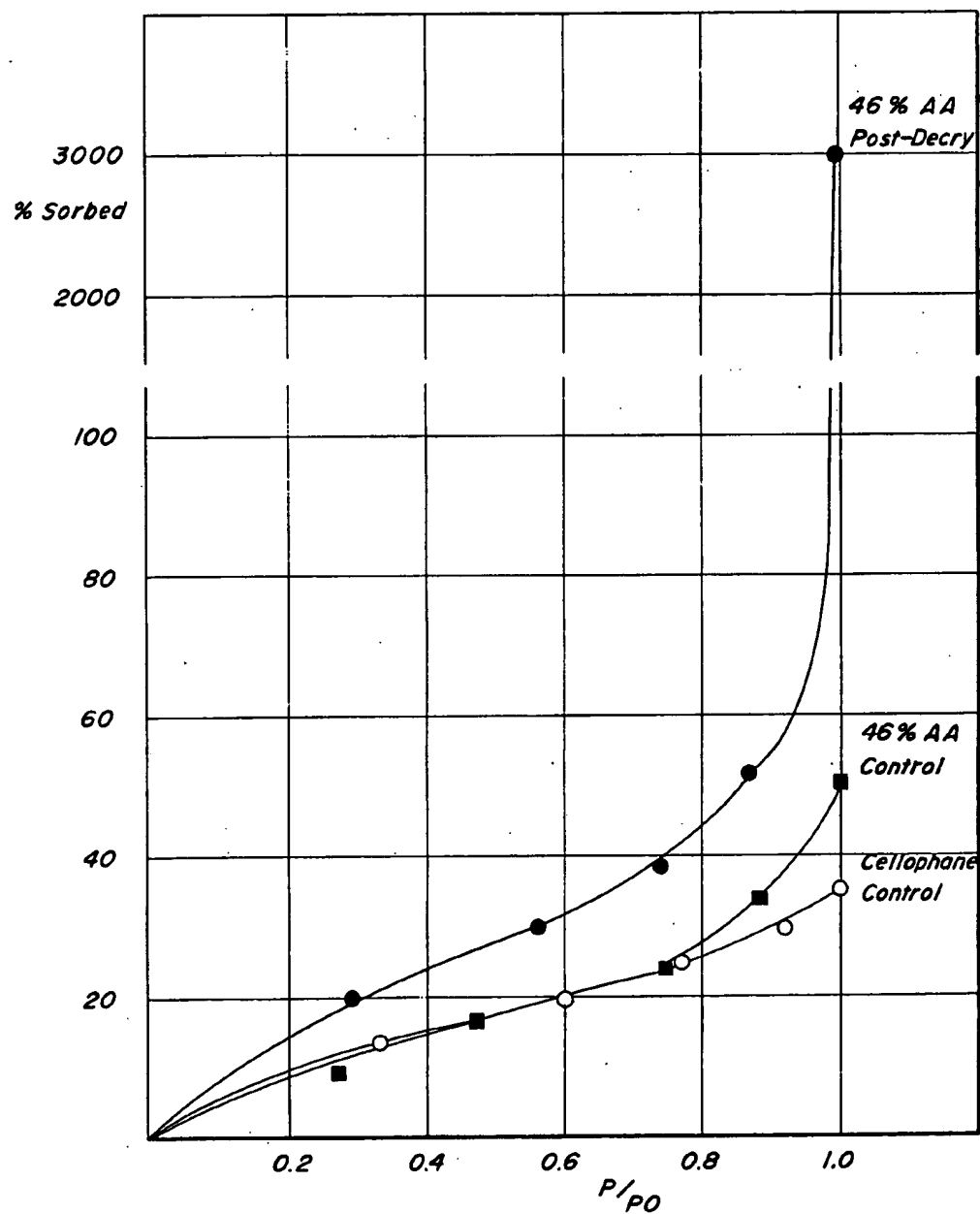
WATER SORPTION ISOTHERMS FOR ACRYLIC ACID GRAFTED RAYON AT 25° C



WATER SORPTION ISOTHERMS FOR ACRYLIC ACID GRAFTED CELLOPHANE AT 25° C

Fig. 1

WATER SORPTION ISOTHERMS FOR
ACRYLIC ACID GRAFTED RAYON
AT 25° C

Fig. 2

WATER SORPTION ISOTHERMS FOR
ACRYLIC ACID GRAFTED CELLOPHANE
AT 25° C

METHOD OF INCREASING THE WATER ABSORPTION OF CELLULOSE-CONTAINING MATERIALS

BACKGROUND OF THE INVENTION

The present invention relates to a method of improving the water absorbent properties of cellulose-containing material.

Numerous methods have been proposed heretofore for increasing the water absorbency or hydrophilicity of cellulose-containing materials. More recently, these efforts have centered around graft-copolymerizing onto the cellulose-containing material monomers containing hydrophilic groups. Following the graft copolymerization step, the hydrophilic groups impart to the material various degrees of water retentive properties.

In the *Journal of Applied Polymer Science*, Vol. 17 (1973) at pages 3143-3156, Lepoutre et al describe a method for increasing the water absorbency of wood pulp by grafting thereon polyacrylonitrile and subsequently hydrolizing the material to a sodium polyacrylate-polyacrylamide copolymer. Williams et al. [*Journal of Applied Polymer Science*, Vol. 10, pages 1229-1245 (1966)] describe a method for modifying the wool-water relationships by grafting techniques. U.S. Pat. No. 3,423,163 to Magat et al describes a method for increasing the moisture absorption properties of cellulose materials by graft copolymerizing thereon N-methylolacrylamide.

U.S. Pat. No. 3,252,880 to Magat et al. discloses that a base polymer may be rendered more hydrophilic by grafting thereon suitable monomeric materials. U.S. Pat. No. 3,514,385 to Magat et al. discloses the grafting of various acrylic compounds to cellulosic base materials in order to increase the hydrophilicity of the resulting product. U.S. Pat. No. 3,201,336 to Magat et al. also discloses grafting acrylic monomers onto cellulosic based materials.

While all of these methods operate to impart some degree of increased hydrophilicity to the materials treated, there has not as yet been proposed a method for drastically increasing the water absorptive properties or hydrophilicity of cellulose-based materials to the extent required in some applications of the cellulose material. For example, a high degree of water absorption is required of disposable diapers comprising cellulose materials. The preparation of catamenial receptors, surgical swabs, etc., also requires the utilization of highly absorptive cellulose materials.

SUMMARY OF THE INVENTION

The present invention provides a method for drastically increasing the water absorptive properties or hydrophilicity of cellulose-containing materials by graft copolymerizing onto said material at least one vinyl monomer containing a hydrophilic group and treating the thus graft-polymerized material with a decrystallizing agent for cellulose in an amount and for a time sufficient to increase the water absorbency of the graft copolymerized material. It has been found that the post-decrystallization step is essential and critical in order to greatly enhance the water absorption properties of the treated material.

DETAILED DESCRIPTION OF THE INVENTION

The cellulose-containing material may be graft-copolymerized with the hydrophilic group containing vinyl monomer according to any conventional method. For example, the graft-copolymerization can be initiated by suitable free-radical initiators such as ceric ion, ferrous ion-hydrogen peroxide, etc. According to the ceric ion method, the cellulose material and vinyl monomer are admixed and contacted with a salt such as ceric ammonium nitrate in an inert atmosphere such as nitrogen for a time sufficient to achieve grafting. In the ferrous ion-hydrogen peroxide initiation process, the cellulose material, a ferrous ammonium sulphate solution of monomer and hydrogen peroxide are admixed in an inert atmosphere such as nitrogen and allowed to stand for a time sufficient to achieve grafting. In the xanthation method the cellulose material is first lightly xanthated with carbon disulfide and sodium hydroxide. The cellulose xanthate is then treated with a trace of ferrous ion salt plus the monomer and hydrogen peroxide. The mixture is then left for sufficient time to achieve the desired degree of grafting.

The preferred method involves exposing the cellulose-containing material to high energy irradiation such as gamma rays from cobalt-60 in a dosage range of from about 0.1 to about 100 megarads, more preferably between about 0.1 and about 50 megarads. Although not essential, best results are obtained where the cellulose-containing material is first subjected to the high energy radiation and then admixed with the vinyl monomer for graft-copolymerization. It is preferred to carry out the irradiation while maintaining the cellulose-containing material under vacuum; however, irradiation can also be carried out under atmospheric conditions. The irradiation results in the formation of free radicals in the cellulose material which are capable of initiating grafting.

Following irradiation, the cellulose-containing material is admixed with an aqueous solution or emulsion of the hydrophilic group containing vinyl monomer. Preferably, the solution or emulsion contains from about 1 to about 80%, by weight, of monomer. Other additives such as dispersing, emulsifying agents, processing agents, etc., may be present in an amount up to about 30% by weight, based on the weight of the solution or emulsion.

Any vinyl monomer, dimer or oligomer capable of graft copolymerization with cellulose and which contains a hydrophilic group may be employed in the practice of the method of the invention. Suitable monomers include those disclosed in the above-cited references. By "hydrophilic group" is meant any group contained in the vinyl monomer which imparts hydrophilicity either to the homopolymerized product or its copolymerization product with a base material such as cellulose. Such hydrophilic groups are well known in the prior art. Suitable monomeric compounds for the practice of the invention include acrylic acid, methacrylic acid, acrylamide, hydroxyethylmethacrylate, vinyl pyrrolidone, vinyl pyridine and mixtures thereof. It is to be understood, however, that any hydrophilic group containing vinyl monomer capable of graft copolymerization with cellulose may be employed in the practice of the invention.

It is preferred to conduct the graft copolymerization to the extent that the cellulosic material contains from

about 30 to about 6000%, by weight, more preferably, from about 30 to about 500%, by weight, of grafted vinyl polymer, based on the weight of the ungrafted cellulosic material. Most preferably, the material contains about 100%, by weight, of the grafted polymer.

Although the graft-copolymerization onto the cellulosic material of the hydrophilic group containing vinyl monomer will result in some increase in hydrophilicity of the material as evidenced by the disclosures of the above-cited references, it is essential in order to radically increase the water absorptive properties of the cellulosic material to decrystallize the material following graft-copolymerization.

Following the graft-copolymerization step, the product is reacted with a decrystallizing agent in an amount and for a time sufficient to increase the water absorbency of the graft-copolymerized material. Generally, the graft-copolymerized product is immersed in an aqueous solution of the decrystallizing agent. Generally, solutions containing from about 15 to about 100 percent by weight of the decrystallizing agent are employed. The graft-copolymerized material is contacted with the decrystallizing agent for a period of time ranging from about 2 to about 120 minutes. Illustrative of suitable decrystallizing agents are zinc chloride, cupriethylene diamine, cupritetramine hydroxide, concentrated liquid ammonia, lithium hydroxide, benzyltrimethylammonium hydroxide, ethylamine, ethylenediamine, solutions of paraformaldehyde in dimethylsulfoxide and solutions of nitrogen tetroxide in dimethylformamide. Where the decrystallizing agents are liquids, the graft-copolymerized product can be contacted directly therewith. Solid decrystallizing agents may be employed as aqueous or other solvent solutions thereof. It is to be understood that the above list of decrystallizing agents is only illustrative and that any agent capable of decrystallizing cellulose may be employed in the practice of the method of the invention. In cases where the decrystallizing agent results in the formation of e.g. copper or zinc salts better absorption is obtained when the material is washed with acid and changed to the sodium or potassium salt with aqueous alkali.

To obtain highly water absorbent materials, it is essential that the decrystallization step be carried out subsequent to the graft-copolymerization step. Where decrystallization is employed prior to grafting, the cellulose will recrystallize during the graft-copolymerization step thereby resulting in a loss of hydrophilicity.

The exact mechanism involved in the method of the present invention is not completely understood. Although not wishing to be bound by any theory of operation, it is hypothesized that the greatly increased water absorption properties of the graft-copolymerized cellulosic material is due to (1) the hydrophilic groups containing in the graft-copolymerized material and to (2) the relative absence of crystalline regions in the cellulose material. Cellulosic fibers are made up of both amorphous and crystalline regions. Water molecules have difficulty penetrating into crystalline regions but penetrate readily into the amorphous regions of the cellulose. The crystalline regions due to strong forces of association resist the swelling action of water. The decrystallization operates to increase the amorphous area of the cellulose material, thereby increasing the water absorptivity.

Also, the graft-copolymerization of the vinyl monomer containing the hydrophilic groups which have an affinity for water results in a division or separation of

the fibrous molecules so that the structure thereof is more susceptible to swelling with water. Furthermore, the bulky polymer chains grafted onto the cellulose prevent the cellulosic chains from recrystallizing when the material is allowed to dry. In any event, both graft co-polymerization with a hydrophilic group containing vinyl monomer and post-decrystallization of the cellulose material is required to achieve a higher degree of water absorption.

The method of the invention is applicable to any cellulose-containing material such as cotton, wood pulp, flax, rayon, cellophane, etc., which may be admixed with any suitable non-cellulosic material and formed into any suitable shape, such as fibers, films, slabs, spheres, etc.

The products produced by the method of the invention possess extremely high water absorption properties while maintaining their mechanical integrity. In addition, the thus treated materials are not "sticky" or "tacky" as is often observed with highly absorbent materials.

The invention is illustrated by the following non-limiting examples:

EXAMPLE 1

0.2 gram of rayon yarn (150 denier) were placed in an evacuated glass ampoule (10^{-5} mm. Hg.) for 24 hours. The samples were then irradiated in a cobalt-60 facility at a dose rate of 0.1 megarads/hours to a total dose of 11.75 megarads at 25° C. during irradiation, the sample was in contact with 20 ml of a degassed solution of 10 ml of acrylic acid and 10 ml of water containing 10^{-2} M CuCl_2 at 25° C. Following irradiation, the samples were removed and washed with water. The samples were then subjected to post-decrystallization by immersion in a 70% solution of zinc chloride in water for 2 hours at 40° C. Subsequently, the samples were washed in water and dried. The samples were found to contain 90% by weight of polyacrylic acid, based on the original weight of the rayon.

The water absorptivity of the graft-copolymerized material, a control sample containing 108% by weight of polyacrylic acid grafted thereon according to the method set forth above but not post-decrystallized and an identical rayon sample which had not been grafted nor decrystallized was determined according to the following procedure:

The sample was allowed to equilibrate in water for 30 minutes and then centrifuged at 500 rpm for 30 minutes. The centrifuge was equipped with a stainless steel frit which allowed the excess water to flow to the bottom of the tube. A cap on the centrifuge tube prevented the relative humidity from dropping below 100%. Finally, the percent of water absorbed was determined by weighing.

A comparison of the water absorption properties of the three samples is shown in FIG. 1. As is apparent, the rayon material treated in accordance with the method of the present invention results in a radically increased hydrophilicity.

EXAMPLE 2

0.2 gram of cellophane film (thickness of 2 mil) were degassed in a glass ampoule at 10^{-5} mm. Hg. for 24 hours and irradiated at 0.1 megarads/hour to a total dose of 9.0 megarads in the presence of 20 ml of a degassed solution of 10 ml acrylic acid and 10 ml of water containing 10^{-2} M CuCl_2 at 25° C. A cobalt-60 facility

was employed, for irradiation. Following irradiation, the samples were washed and dried and found to contain 46% by weight of polyacrylic acid grafted thereon. The samples were then subjected to a 70% zinc chloride solution for 2 hours at 40° C. and washed.

The water absorption properties of the samples, as well as a similar sample which had been identically grafted but not post-decrystallized, and an equivalent amount of identical cellophane film were determined. The results are illustrated in FIG. 2. As is apparent, the cellophane film treated in accordance with the method of the invention has a high degree of water absorptivity as compared with the non-decrystallized material and the untreated cellophane material.

EXAMPLE 3

0.2 gram of rayon identical to that employed in Example 1 was graft-copolymerized with acrylic acid according to the manner described in Example 1. Following grafting, the samples were subjected to post-decrystallization employing a 25% solution of cupriethylene diamine for 15 minutes and then rinsed and dried. The sample was found to imbibe greater than 3200% by weight of water.

EXAMPLE 4

The procedure of Example 2 was followed except that the graft-copolymerized sample was post-decrystallized with a 25% solution of cupriethylene diamine for 15 minutes and then rinsed. The sample was found to be capable of absorbing in excess of 2800% by weight of water.

EXAMPLE 5

Cellophane film (0.2856 grams) was placed into a glass ampoule. A solution of 5 ml acrylic acid and 5 ml 0.06 M $K_2S_2O_8$ (Potassium Persulfate) was added and diffused under vacuum. The sample was allowed to react in a thermostatted bath at 25° C for 24 hours. Afterwards, the sample was washed, dried, and weighed. Following grafting, the percent graft was determined to be 134% by weight. The sample was then subjected to post-decrystallization using Zinc chloride in water (7 gms $ZnCl_2$ + 3 ml H_2O) for 2 hours. Following decrystallization, the sample was found to absorb 2500% water according to the method outlined in Example 1.

EXAMPLE 6

Rayon yarn (0.21 grams) was grafted in a similar fashion as cellophane described in Example 5. After grafting, the sample was found to contain 252% graft. After post-decrystallization for 2 hours in 70% $ZnCl_2$ (7 gm $ZnCl_2$ + 3 ml H_2O) the sample absorbed in excess of 2200% water.

EXAMPLE 7

Cellophane film (0.20 grams) was placed in a nitrogen flushed bottle containing 5 ml acrylic acid, 10^{-4} moles of $FeSO_4$, and 2×10^{-4} moles H_2O_2 , buffered to pH of 4.6. The sample was allowed to graft for 2 hours at 30° C. Afterwards, the grafting was determined to be 124% by weight. The same was then post-decrystallized for 2 hours in 70% $ZnCl_2$ (7 gm $ZnCl_2$ + 3 gm H_2O). Following decrystallization the sample was found to absorb in excess of 2600% water.

EXAMPLE 8

2.0 grams of cotton fabric was xanthated for 20 minutes at 25° C. in a solution containing 40 grams of 5% $NaCH_3$, 2.8 grams CS_2 , and 1.0 grams of Triton X-405. Afterwards, the sample was water washed and subsequently soaked in water containing 6 ppm of iron (Ferrous ammonium sulfate) for 15 minutes at 25° C. The sample was then washed, dried, and placed in a grafting solution containing 35.8 grams H_2O , 0.23 grams H_2O_2 , and 18.3 grams methacrylic acid. The sample was allowed to graft in a sealed tube at 50° C. for 7 minutes. Following grafting, the sample was washed in water and dried. The sample was weighed and found to contain 58% graft based on the original weight of the fabric.

The sample was then subjected to post-decrystallization using zinc chloride in water (7 grams $ZnCl_2$ + 3 ml H_2O) for 2 hours. Following decrystallization, the sample was found to absorb 2400% water according to the method described in Example 1.

EXAMPLE 9

The procedure of Example 8 was followed except the grafted sample was post-decrystallized with a 25% solution of cupriethylene diamine for 30 minutes and rinsed. The sample was found to absorb 2600% water following decrystallization.

We claim:

1. In a process for imparting water-absorbent properties to a cellulose-containing material by graft-copolymerizing onto said material at least one vinyl monomer containing a hydrophilic group the improvement comprising treating said graft-copolymerized material with a decrystallizing agent for cellulose in an amount and for a time sufficient to increase the water absorbency of the graft copolymerized material.
2. The process of claim 1 wherein said graft-copolymerization is effected in the presence of high energy radiation.
3. The process of claim 2 wherein said material is subjected to high energy radiation prior to said graft-copolymerization.
4. The process of claim 3 wherein the irradiation dose is in the range of 0.1 to 100 megarads.
5. The process of claim 3 wherein the irradiation dose is in the range of 0.1 to 50 megarads.
6. The process of claim 1 wherein said vinyl monomer is selected from the group consisting of acrylic acid, methacrylic acid, acrylamide, hydroxyethylmethacrylate, hydroxy ethyl acrylate, vinyl pyrrolidone, vinyl pyridine, vinyl alkyl ether, maleic anhydride, poly maleic acid half esters, polystyrene sulfonic acid.
7. The process of claim 1 wherein the amount of vinyl monomer copolymerized onto said material is at least 30% by weight, based on the weight of the material.
8. The process of claim 1 wherein the decrystallizing agent is selected from the group consisting of zinc chloride, cupriethylene diamine, cupritetramine hydroxide, concentrated liquid ammonia, lithium hydroxide, benzyltrimethylammonium hydroxide, ethylamine and ethylenediamine, a solution of paraformaldehyde in dimethyl sulfoxide and nitrogen tetroxide in dimethyl formamide.
9. The process of claim 1 wherein said cellulose material is rayon. graft-copolymerization.
10. The process of claim 1 wherein said cellulose material is cotton.

11. The process of claim 1 wherein said cellulose material is cellophane.

12. In a process for imparting water-absorbent properties to a cellulose-containing material by graft-copolymerizing onto said material at least one vinyl monomer containing a hydrophilic group, the improvement comprising effecting said graft-copolymerization after irradiating said material with a dose of 0.1 to 100 megarads of high energy radiation and then treating said material with a decrystallizing agent for cellulose in an amount and for a time sufficient to increase the water-absorbency of the graft-copolymerized material, wherein the amount of vinyl monomer copolymerized

onto said material is at least about 30%, by weight, based on the weight of the material.

13. The process of claim 1 wherein said graft-copolymerization is effected in the presence of a free-radical initiator.

14. The process of claim 13 wherein said initiator is ceric ion.

15. The process of claim 13 wherein said initiator is ferrous ion-hydrogen peroxide.

16. The process of claim 13 wherein the initiation is achieved by xanthation followed by treatment with ferrous ion and hydrogen peroxide.

17. The product produced according to the process of claim 1.

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